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LASER INDUCED REACTION FOR PREBOND SURFACE PREPARATION OF ALUMINUM ALLOYS

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Annual Report (4/93-12/94)
Contract No. F61708-93-C005

by

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CONTENT

1. INTRODUCTION

The potential of UV lasers irradiation as prebonding treatment of Al-2024 alloy was proved in a previous investigation(1) using a modified epoxy adhesive(2).
Surface treatment of Al by excimer laser results in oxidation and morphological changes of the surface promoting shear adhesion strength when optimal laser conditions are applied. The adhesion strength achieved by the laser treatment is similar or higher compared to chemically treated Al.

The objective of this research is to establish the effect of excimer ArF UV laser on the Al alloy surface microstructure and activity and to find its correlation with the macro behavior of shear strength,tensile strength, resistance to peel and failure locus. The treated system was adhesively bonded with structural adhesives and durability tests were performed.

Structural adhesives are used in bonding and repairing processes for aerospace application.Surface treatment for bonding Al adherends with structural adhesives involve the use of harsh chemicals such as acids, bases and organic solvents.Laser surface irradiation can therefore be used as an alternative, ecologically favorable treatment. In order to achieve high adhesive strength optimal laser parameters for preadhesion surface treatment specified for each adhesive should be chosen including repetition rate,energy and irradiation time (no. of pulses).

The five stages of this research are included in this annual report (April 93-December 94).

The first stage of this research (001 of the contract) included the preparation of all the Al specimens with the required configurations for the various mechanical and environmental tests.

The second stage of this research (0002 of the contract) determined the correlation between the various laser parameters used for surface treatment and the adhesive shear strength in order to achieve the maximum ashesive strength for the various structural adhesives specified in the first stage (0001 of the contract). The effect of the time interval between laser irradiation and adhesive bonding (open time) was also investigated in this stage.

The third stage of this research (0003 of the contract) included the characterization of the failure modes of the various joints tested in shear and the chemical changes occurring on the Al substrate after irradiation. The results of the shear strength which were reported in the previous (second) stage are presented again in conjunction with the morphological results.

The fourth stage of this research (0004 of the contract) included the results of the tensile and the peel tests of laser treated aluminum specimens bonded with various structural adhesives, and initial durability tests including exposure of the specimens to humidity and extreme temperatures.

The fifth stage of this research (0005 of the contract) included durability evaluation by wedge test and extended shear tests in hostile environments(60^0c, 95% RH humidity). Another task achieved in this stage was a vacuum system which was designed and ordered in order to enable the investigation of the effect of various atmospheres on laser prebond treatment.

2. EXPERIMENTAL

2.1 Laser Treatment

The laser used during the course of this investigation was a UV excimer ArF (193 nm) laser EMG 201 MSC manufacture by "Lambda Physik", Germany. The Beam cross section was 20x5mm with an energy of 200mj/p*cm². Higher laser energies were achieved by reducing the laser beam area using a focusing lens. Repetition rate was 30Hz and the number of pulses ranged between 1-5000.
Scanning was done by moving the specimen by means of a controlled x-y-z table. A special computerized table was designed and built in order to provide suitable velocities for continuous scanning. All experiments were conducted at ambient temperature and room environment. Fig 2.1 shows schematic drawing and photo of the irradiation system.

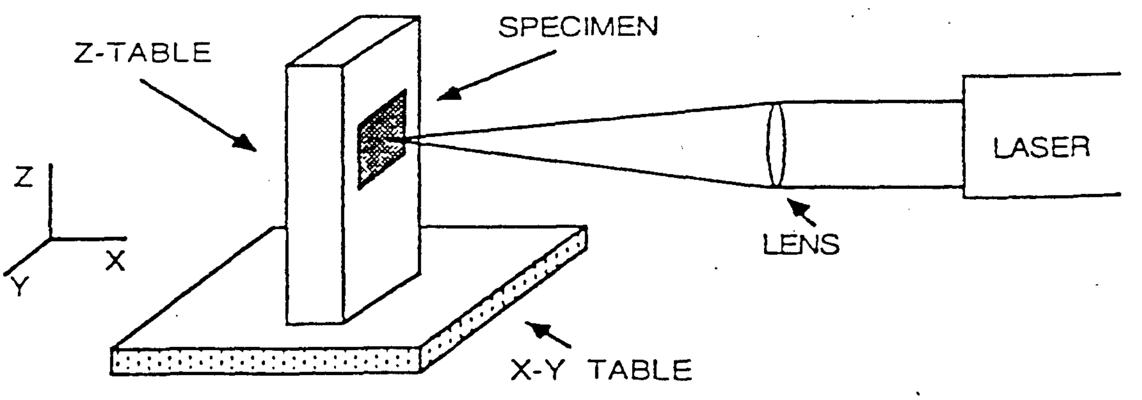


Figure 2.1a: A schematic drawing of the irradiation system

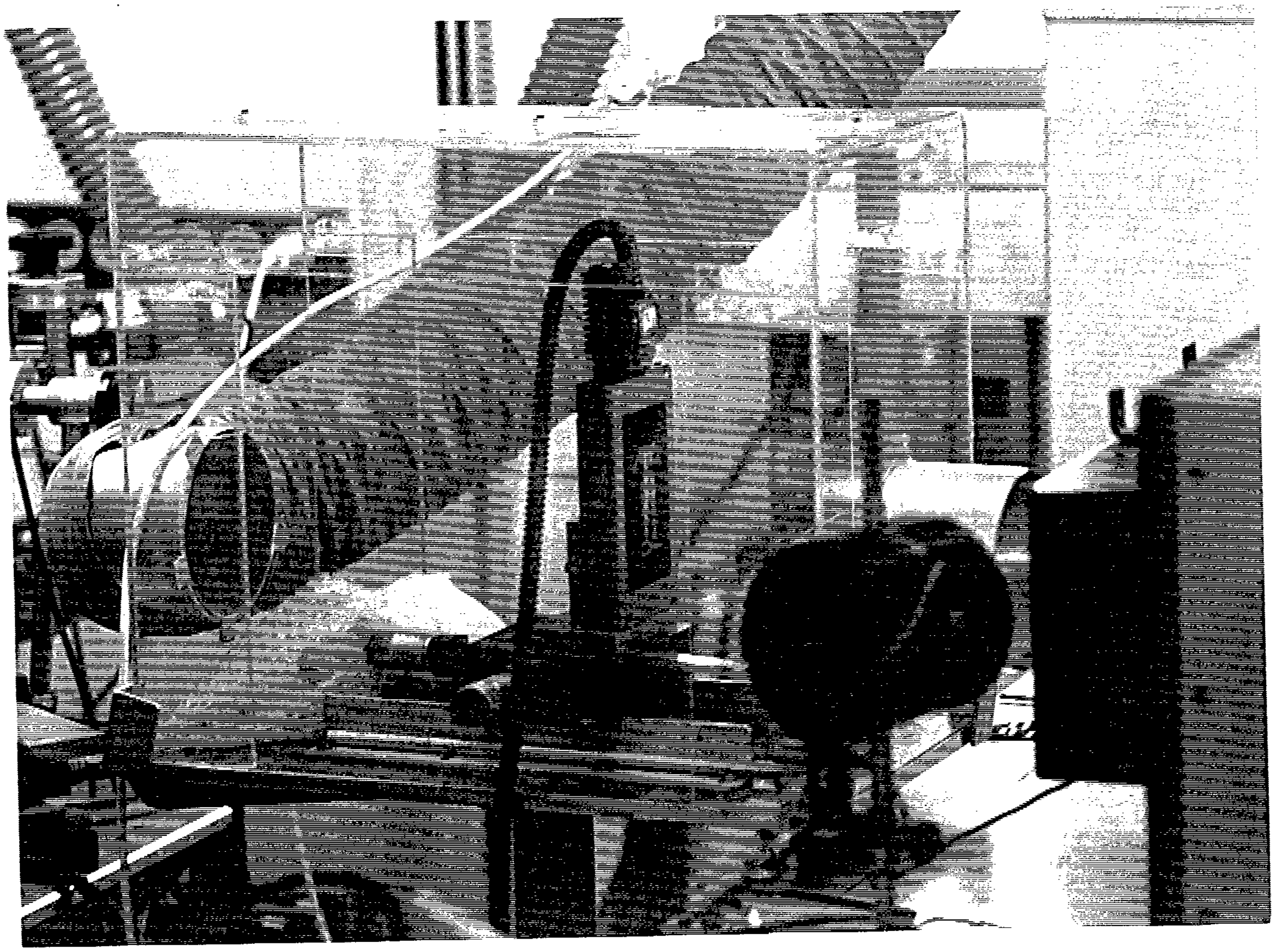


Figure 2.1b: Photograph of the irradiation system

2.2 Adherend and Adhesives

The adherends used throughout this work were Al 2024-T3. Irradiated specimen were bonded by three different structural adhesives after primer application. Table 2.1 summarizes the data of the applied adhesives and primers.

Table 2.1: The structural adhesives and primers

COMMERCIAL NAME (CYANAMID)	CURING CONDITIONS	APPLICATION FORM	SERVICE TEMPERATURE RANGE
FM73	1 Hr. 120°C 40psi	FILM,0.38mm POLYESTER CARRIER	-55°C to +120°C
FM3002K	1.5Hr. 120°C 40psi	FILM,0.3mm POLYESTER CARRIER	-55°C to +175°C
FM350NA	1Hr. 177°C 30psi	FILM GLASS CARRIER	-65°C to +177°C
BR127 (chromate base)	1/2Hr. R.T 1/2Hr. 121°C	MIXING,BRUSHING	-55°C to +177°C
A187 (silane)	1/2Hr. R.T 1/2Hr.90°C	BRUSHING 2cc A187 in 80cc ethanol and 20cc D.I. water	- NA -
BR154	1Hr. R.T 1Hr. 177°C	BRUSHING	-55°C to +177°C

2.3 Testing

Adhesive joints properties were determined using various techniques:
Single Lap Shear joints (SLS) according to ASTM D-1002-72 (see fig.2.3).
T peel joints according to ASTM D-3167 (see fig.2.4).

Flat wise (FW) tensile joints according to ASTM C-297 (see fig. 2.5).

Single Lap Shear joints (SLS) were also used to study the effect of extreme temperatures and heat/humidity (60°c,95%RH for 10 days) on the laser treated and bonded adherends.

Durability wedge tests were conducted according to ASTM D-3762 (see fig 2.6). The specimen were exposed to hygrothermal conditions (60°C, 95%RH) in a humidity chamber. The advance of the initial crack length was measured as a function of exposure time (at 1,4,24 and 164 hours). At the end of the test the adherends were forced open and the mode of failure was determined.

The mode of failure was determined to be either adhesive (locus of failure at adhesive/substrate interface) or cohesive (locus of failure in the adhesive bulk).
The surface of the irradiated area before bonding and the fracture surface morphology after failure were studied by Scanning Electron Microscope (SEM) (Jeol model JMS 840, Japan) equipped with Energy Dispersive System (EDS, Link model 290).

The surface chemical composition of laser treated adherends was examined and compared to untreated ones by FTIR (Fourier Transform Infra -Red) spectrophotometer (Nicolet 5DX) in external specular mode, and by AUGER Electron Spectroscopy (AES) (Physical Electronic Ind. model 590A).

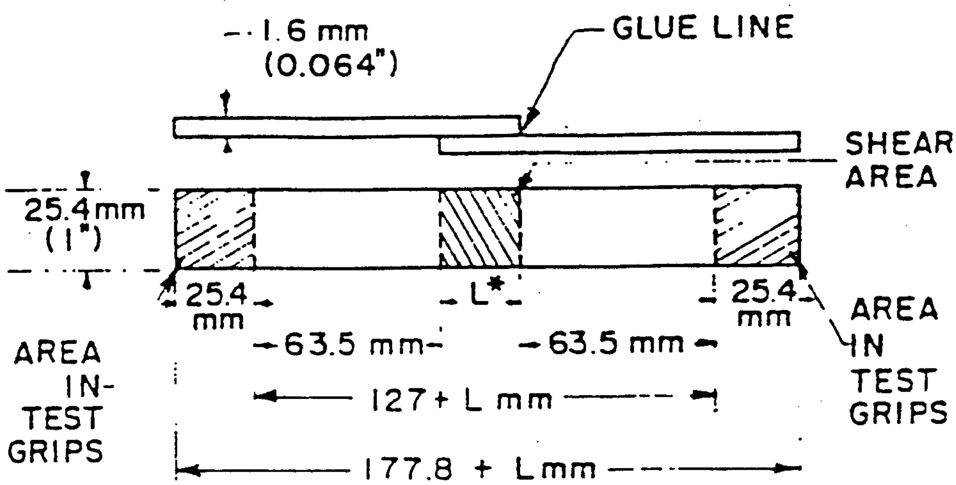
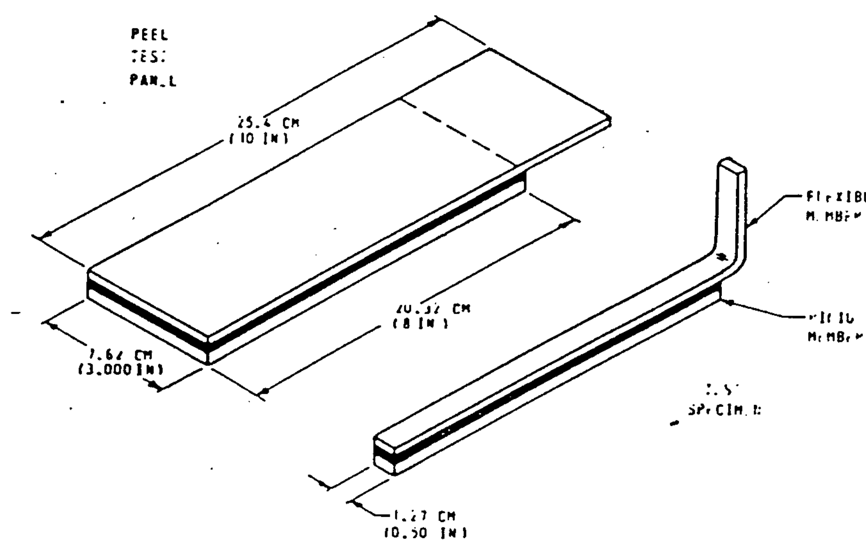


Fig.2.3: SLS joints.



NOTE—A 1.5 to 3.0-in. (38.1 to 74.2-mm) shim can be used to facilitate the start of peel.

Fig. 2.4: Peel tests joints.

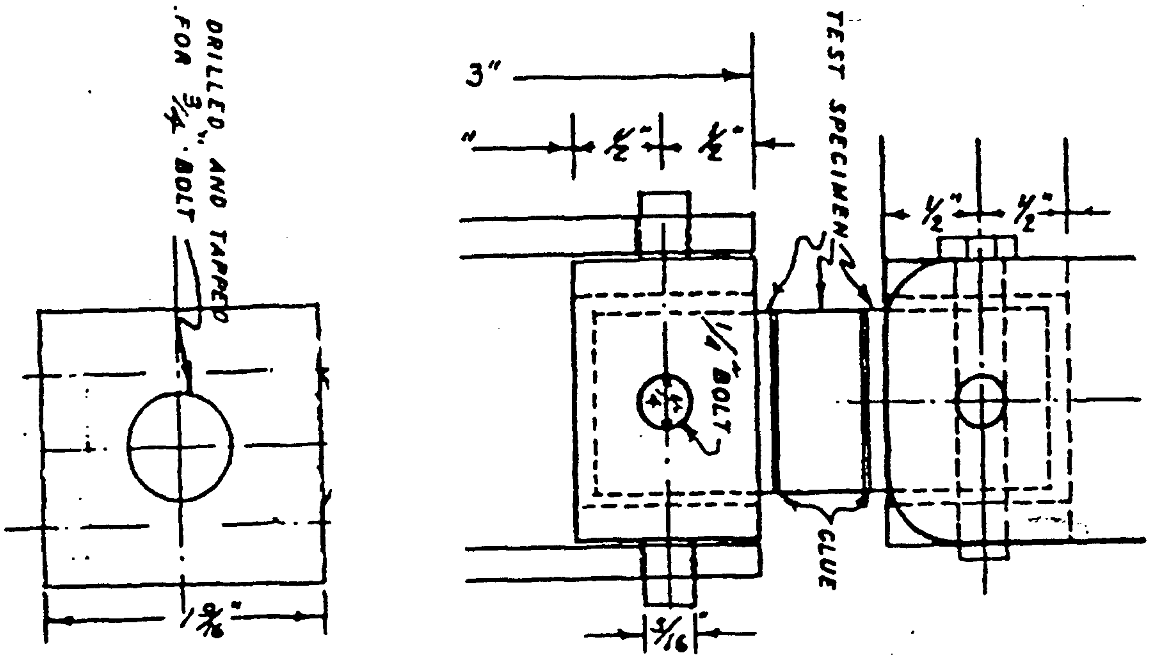


Fig. 2.5: Tensile tests joints.

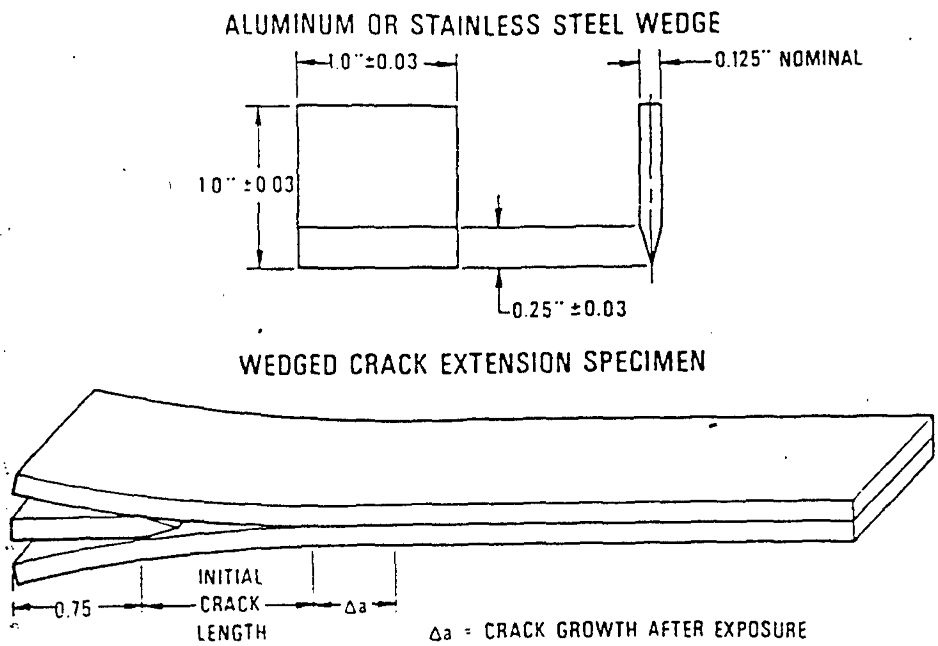


Fig.2.6: Wedge tests joints.

2.4 Methodology

Two kinds of references were used in all the experiments for comparison with of laser treated specimens: a non-treated Al 2024-T3 and an unsealed chromic acid anodized Al (according to MIL-A-8625C).The second reference is a conventional prebonding treatment for aluminum alloys. The reference joints were tested with the same adhesives and primers as the laser treated ones. Primer application was carried out immediately after laser irradiation. Usually the adherends were kept in a desiccator between primer application and bonding,except for the investigating of open time in which the adherends were wrapped in paper and stored in room environment.

2.5: Close System design

In order to investigate the effect of various environments on laser treatment a vacuum system was designed and ordered. The vacuum system should meet the following requirement:

a: Working at a basic pressure of 10^{-6} mbar and total pressure up to 2 bar.

b. Fully dried system (without oil) suitable for corrosive environment.

c. Big enough system to contain SLS adherends with an optional xy table.

d. A pyrex treatment chamber in order to see the laser effect

e. Reaching the base pressure as quickly as possible (about 1hr.)

f. Easy to handle and operate.

g. Various feed opening for gauges and gas connection

h. Price limit.

The system that fulfilled these requirements was suggested by SASKIA Inc. from Germany (fig2.7).The system includes a membrane pump as backing to a turbomolecular pump with a boster pump. The chamber is a pyrex cylinder with top and bottom aluminum coated Ni plates.

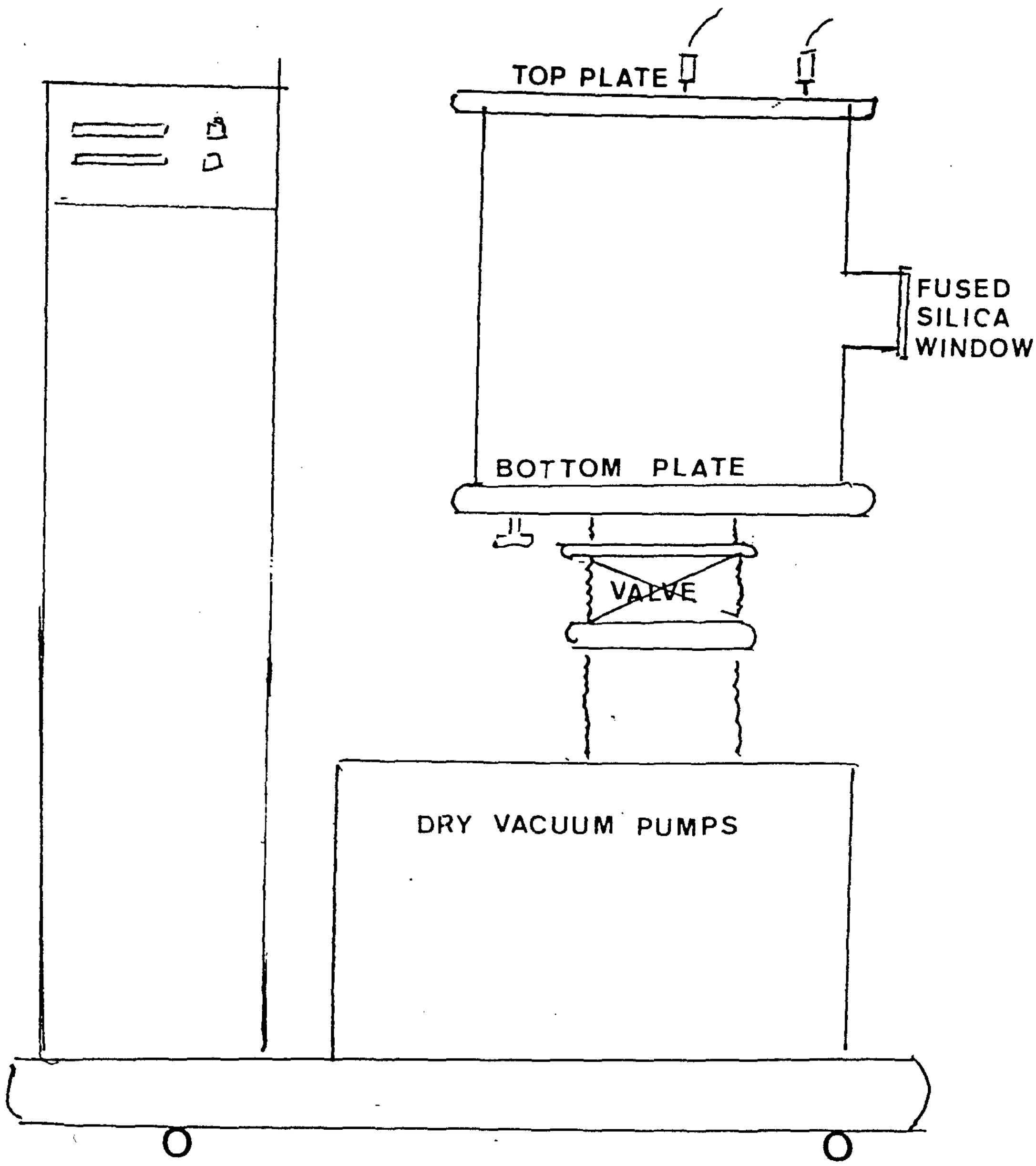


Fig. 2.7: Close system design.

3. SUMMARY OF THE RESULTS.

3.1 Optimization of irradiation conditions for adhesive bonding with structural adhesives. Mechanical SLS Results

Investigation of the effect of prebonding surface treatment with excimer laser on bond strength of three structural adhesives was carried out. Adhesive bonding joint strengths were determined using Single-Lap-Shear joints (SLS).

The adhesion strength with laser treated adherends was improved by more than 150% compared to adhesion strength of untreated Al, and was close to the shear strength of unsealed chromic acid anodized Al. Table 3.1 summarizes the highest values of shear strengths achieved with the optimal laser parameters (see detailed tables of results from the previous reports in appendix A).

The shear strength values after laser treatment of Al 2024 adherends and application of the primer A187, bonded with the adhesives FM73,FM300 2K were similar to those obtained with unsealed anodization treatment and were high enough to be suited for structural bonding.The highest values obtained were 344Kg/cm^2 with FM73 and 294Kg/cm^2 with FM300 2K, compared to those of the anodized adherends (394Kg/cm^2 and 306Kg/cm^2,respectively) (chap. 3.1 stage 2 report).

The shear strength of laser treated joints with A187 and FM350NA was 217Kg/cm^2 compared to 153Kg/cm^2 with the primer BR154 and FM350NA. The anodized joints had shear strengths of 231Kg/cm^2 and 249Kg/cm^2 with FM350NA using the primers BR154 or A187, respectively (chap.3.4 stage four report).

Failure modes for laser treated joints were cohesive for FM73 and FM300 2K and adhesive for FM350NA (fig 3.1).

The reason for the lower performance of FM 350NA with laser treatment resulted from the higher temperatures used in the application of this adhesive. The effect of high temperature on laser treatment will be investigated in a future research and temperature limits will be determined.

According to the SLS results the highest shear strengths were obtained for the adhesives FM73 and FM3000 2K at a laser energy of $0.18 j/p*cm^2$ and 2000pulses or scanning velocity of 2.7mm/min at 30Hz. For FM350NA the highest shear strengths were found at laser energy of $0.18 j/p*cm^2$ with 600pulses or scanning velocity of 8.9mm/min at 30Hz. (chap. 3.1 stage 2 report, chap.3.4 stage four report) .

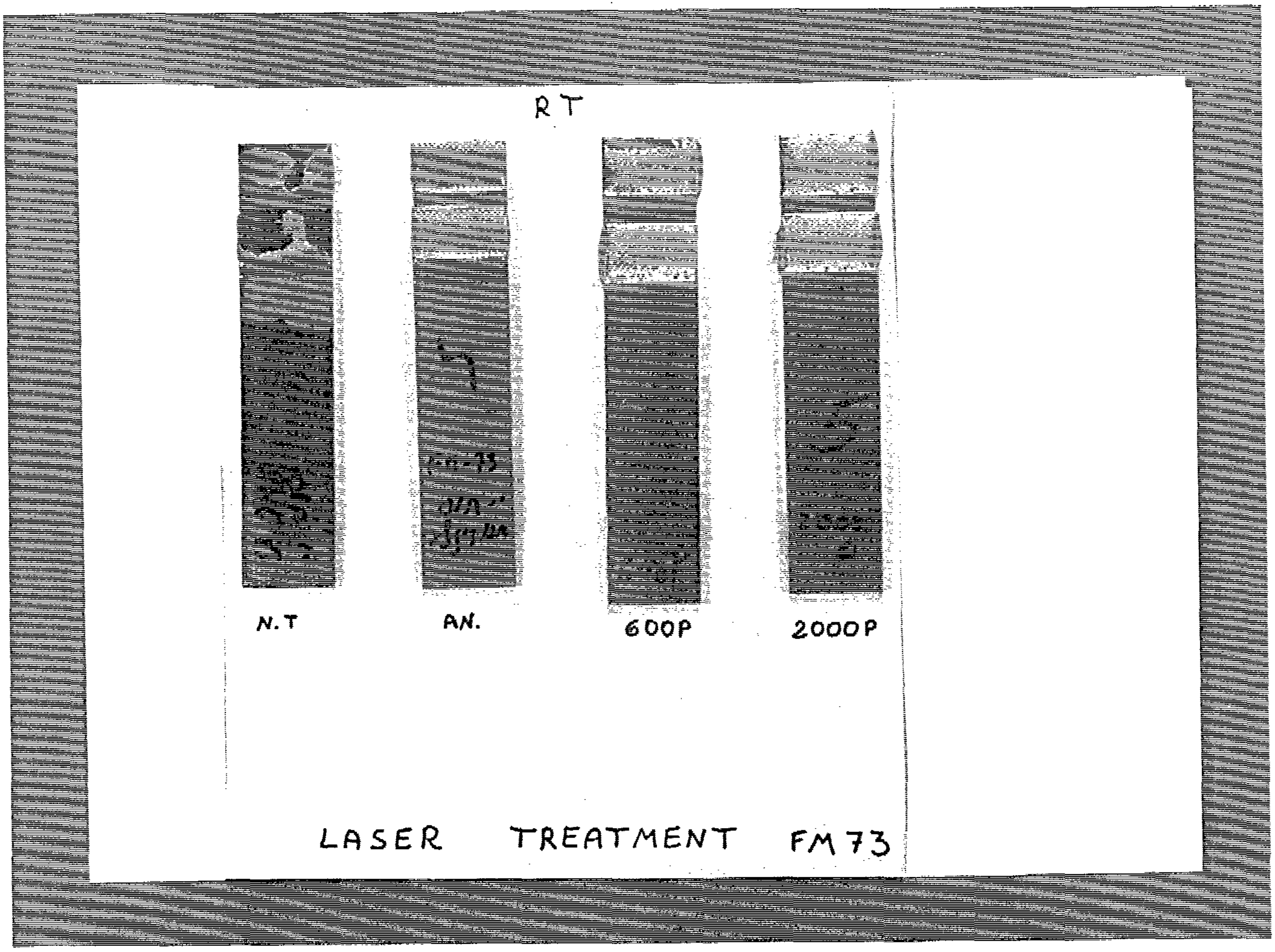
Applying the primers BR127 and BR154 with the adhesive FM350NA did not improve the shear strength probably due to etching of the fine morphology created by the laser treatment on the surface of the adherend.
Silane A187 was more suitable as a primer following laser irradiation for the three adhesives(FM73, FM300 2K and FM350NA) .

The advantages of A187 are: homogeneity, thin layer application and no etching of anodization (water base). This primer reacts chemically with the aluminum oxide of the adherend and the epoxide group of the adhesive through its end groups(3). A187 is a water based primer which does not contain acids or chromate particles as in the case of BR127 thus being ecologically favorable .

Table 3.1: The highest shear strengths obtained for the various structural adhesives.

ADHERENDS	ADHESIVE	PRIMER	SHEAR STRENGTH Kg/cm^2	FAILURE MODE	LASER ENERGY $J/P*cm^2$	PULSE NO.
UNTREATED	FM73	A187	303	C	-	-
ANODIZED			394	C	-	-
LASER TREATED			344	C	0.18	2000
UNTREATED	FM73	BR127	128	C	-	-
ANODIZED			428	C	-	-
LASER TREATED			329	C	0.18	1000
UNTREATED	FM300-2K	A187	-		-	-
ANODIZED			-		-	-
LASER TREATED			294	C	0.18	1000
UNTREATED	FM300 2K	BR127	39	A	-	-
ANODIZED			305	M	-	-
LASER TREATED			101	A	0.18	2000
UNTREATED	FM350NA	A187	103	A	-	-
ANODIZED			249	A	-	-
LASER TREATED			217	A	0.18	1000
UNTREATED	FM350NA	BR154	124	A	-	-
ANODIZED			231	A	-	-
LASER TREATED			153	A	0.18	600
UNTREATED	FM350NA	BR127	55	A	-	-
ANODIZED			264	C	-	-
LASER TREATED			92	A	0.18	600

C - cohesive failure
A - adhesive failure
M - mixed failure



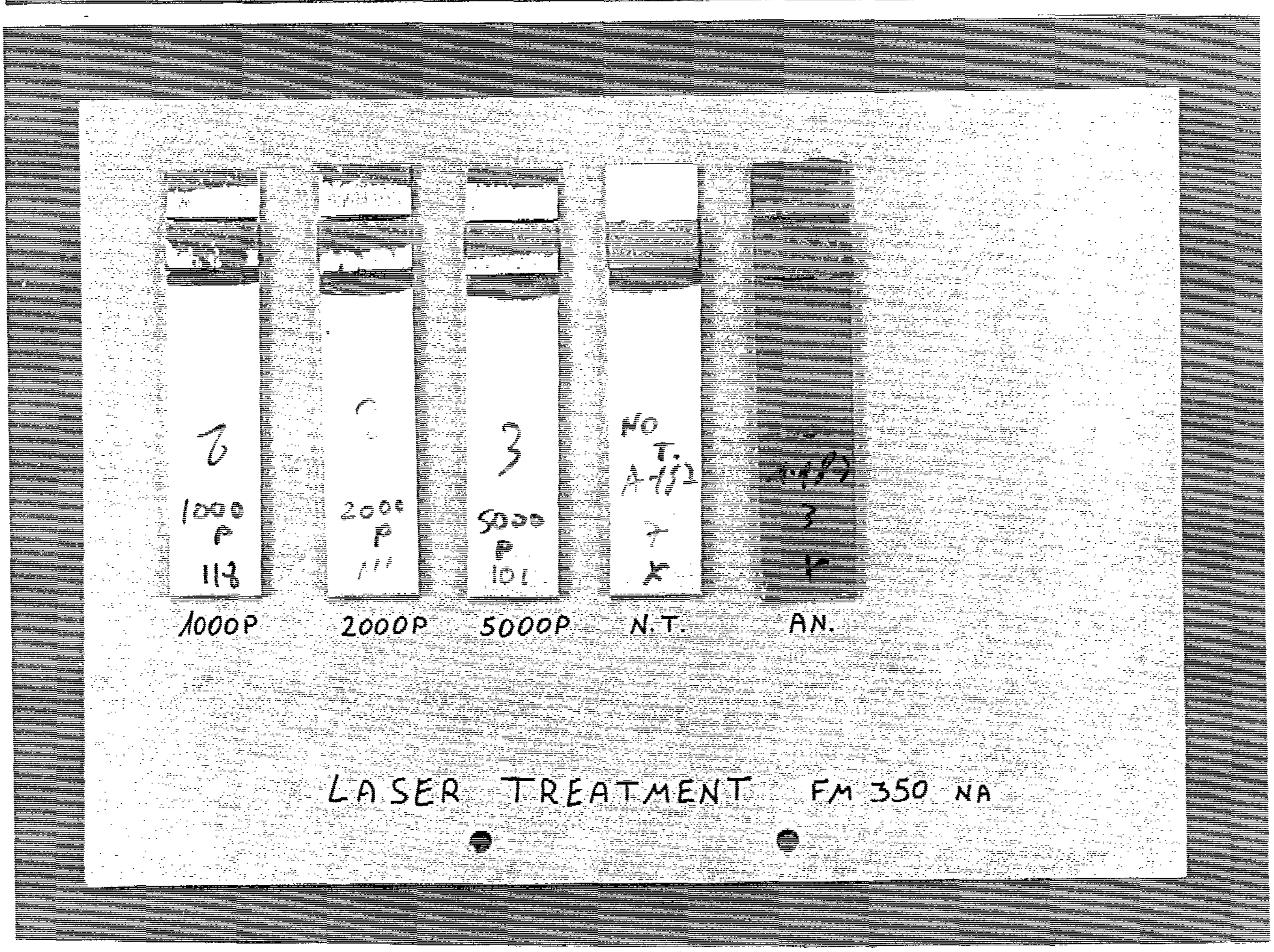


Figure 3.1:View of failure mode for a:adhesive FM73 and primer A187 , b: adhesive FM350NA and primer A187.

3.2: Failure Mode and Surface Morphology after Shear tests.

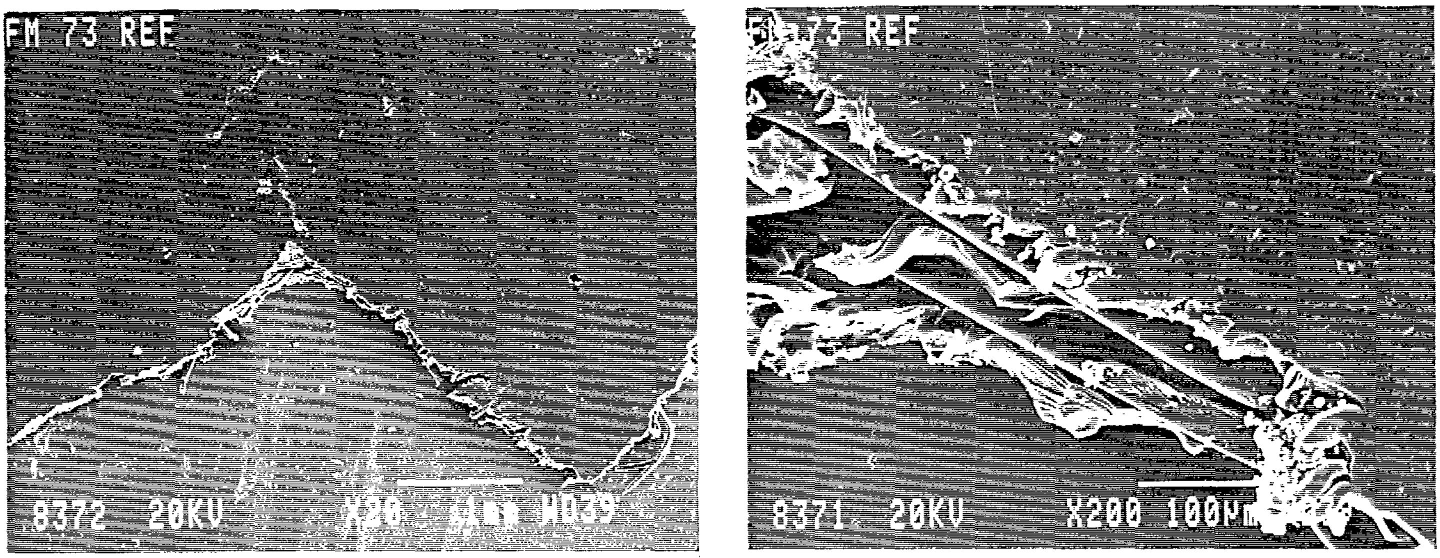
Failure modes of laser treated surfaces were studied with SEM. Chap. 3.1 of stage 3 report summarizes the SEM observations of fructured surfaces after SLS tests. Fig. 3.2 shows typical SEM micrographs of adhesive (a) and cohesive (b) modes of failure.
The cohesive failure is localized within the adhesive.
The carrier net and the matrix of the adhesive are present on both surfaces of the adherends.
The adhesive failure is localized in the interface between the adhesive and the aluminum adherend. The metal surface was exposed on one side and a smooth surface of the adhesive was observed on the opposite side.

The adhesive failure is typical for an untreated adherend treated with the primer BR127 and bonded with the adhesive FM73 while the cohesive failure is typical for an anodized adherend with the same adhesive and primer.
Laser treatment results in a similar cohesive failure as the anodized adherend when bonding with FM73 and primer BR127 (fig. 3.2c).

Figs. 3.2d,e,f show the surface morphology of laser treated joints with the adhesive FM300 2K and the primer BR127. The failure is a mixed mode.

A similar mixed failure mode of the laser treated joints with FM350NA and primer A187 as shown in fig. 3.2g.

a.



b.

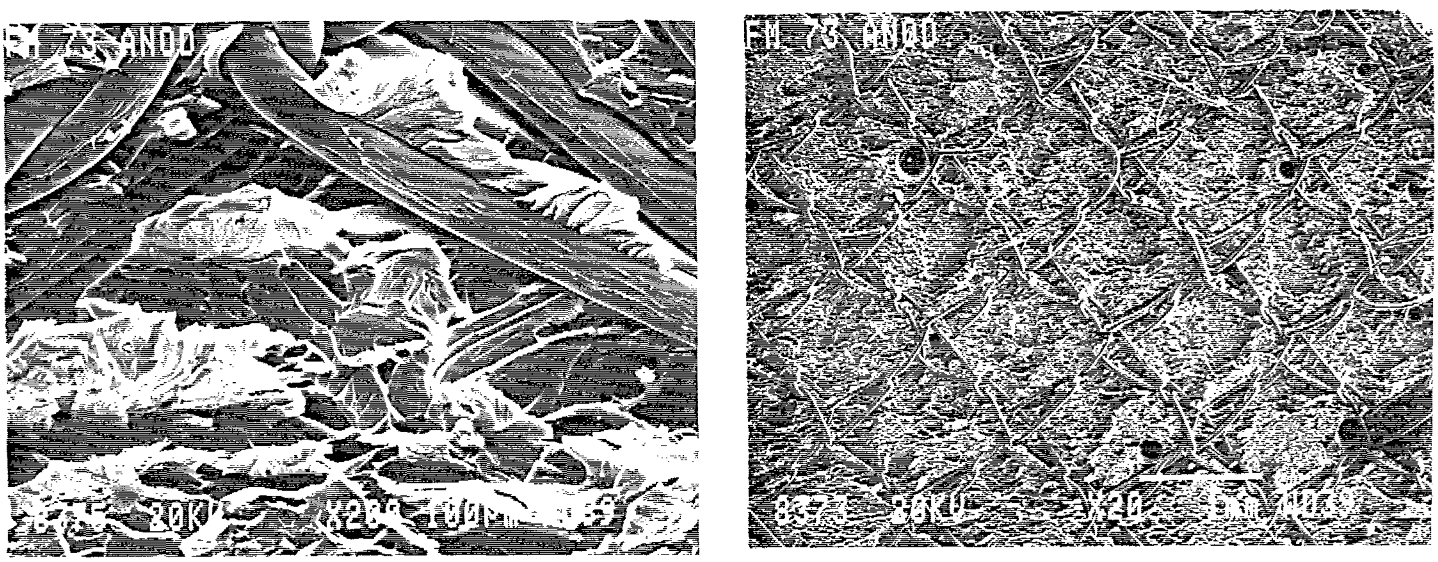
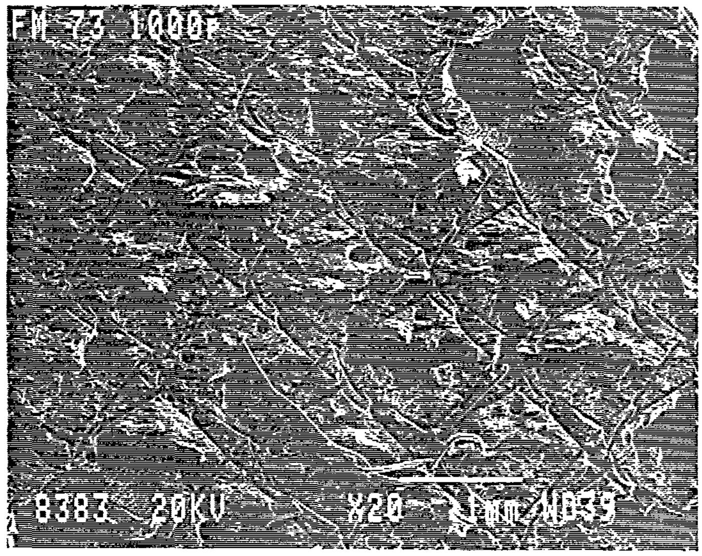


Fig. 3.2: SEM micrograph of the surface failure morphology of SLS joints, with the adhesive FM73 and primer BR127. a: without treatment. b: anodized adherends. c:laser treated.



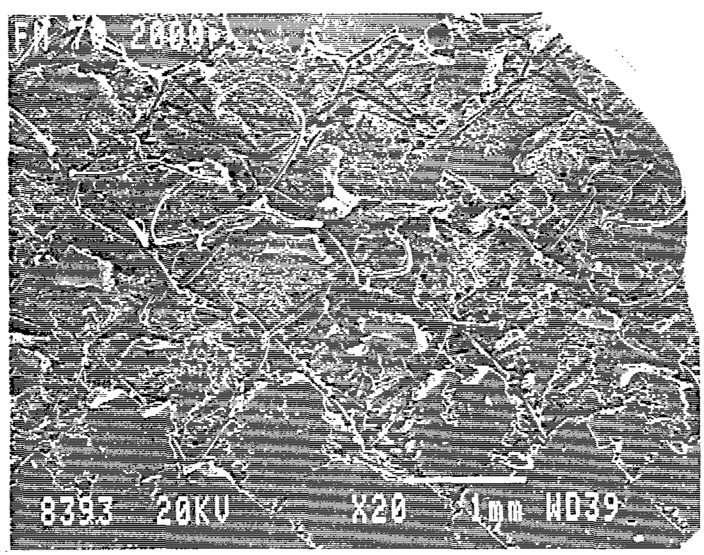
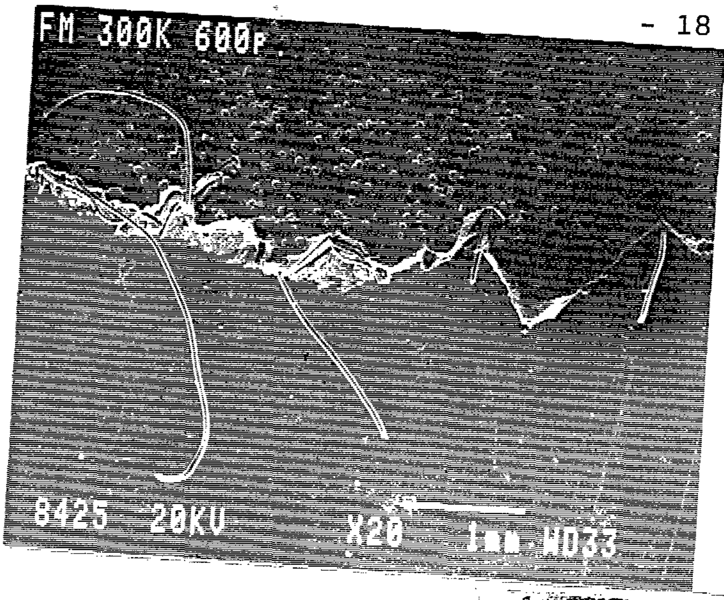
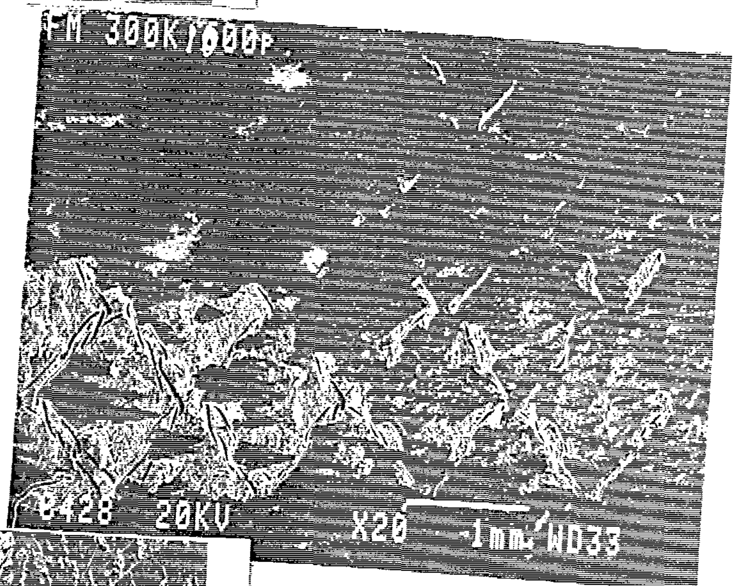


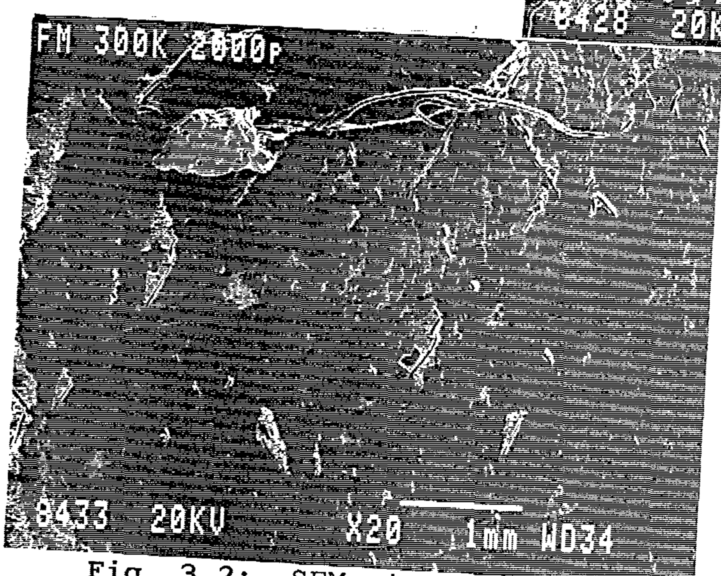
Fig. 3.2c: SEM micrographs of the surface failure morphology of SLS joints,with the adhesive FM73 and primer BR127, laser treated at 2000 pulses, 180mj/p*cm².



d.

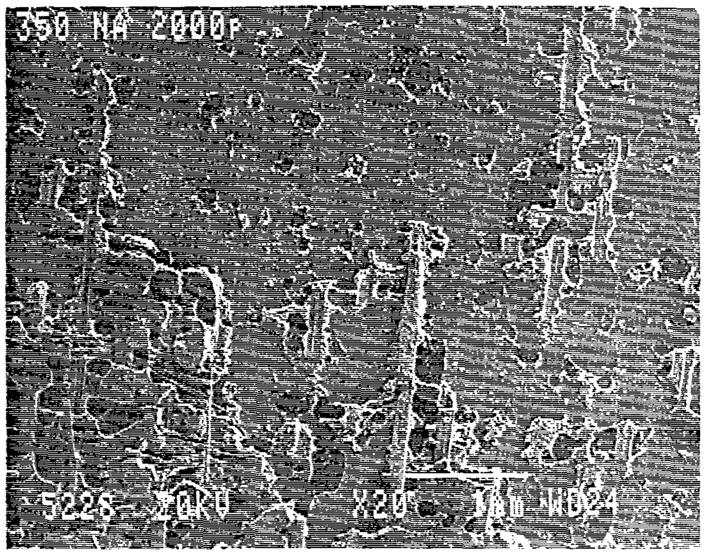


e.



f.

Fig. 3.2: SEM micrographs of the surface failure morphology of SLS joints with the adhesive FM3002K, primer BR127, laser energy 180mj/p*cm² d: laser treated adherends, 600 pulses. e: laser treated adherends, 1000 pulses. f: laser treated adherends, 2000 pulses.



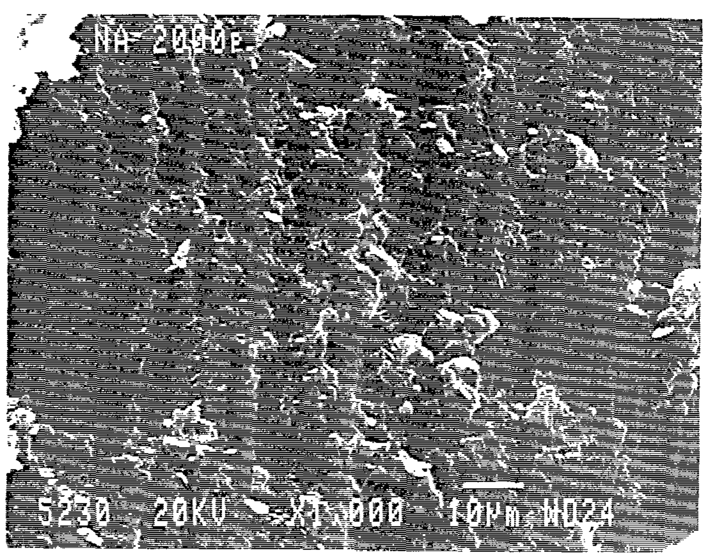


Fig. 3.2g: SEM micrographs of the surface failure morphology of SLS joints with these adhesive FM350NA, primer A187, laser energy 180mj/p*cm², 2000 pulses.

3.3: Effect of "Open time" between Irradiation and Adhesive bonding.

Al adhesives were laser treated with optimal parameters (180mj/p,2000p) and stayed exposed for various periods of time till bonding with FM73. Application of primer directly after laser treatment was compared to non primerd adherends.
Shear adhesion strength and mode of failure were studied.

Fig.3.4 shows the results of both series of joints at various "open times".
It can be observed that after 4 days of exposure the joints strength increases probably due to relaxation effects. A similar effect was found for laser treated thermoplastic adherends.
For non primed adherends open time is about 10-12 days while adhesive bonding can be applied even 20 days after laser treatment providing that primer was applied immediately after laser irradiation. Fig 3.4 shows the fractured adherends after SLS tests while fig. 3.3 presented the shear strength results. It can be clearly seen that for laser treated and primed adherends failure mode , even after 20 days of exposure is still cohesive, while for non primed adherends the failure becomes mixed after 10 or more days of exposure.

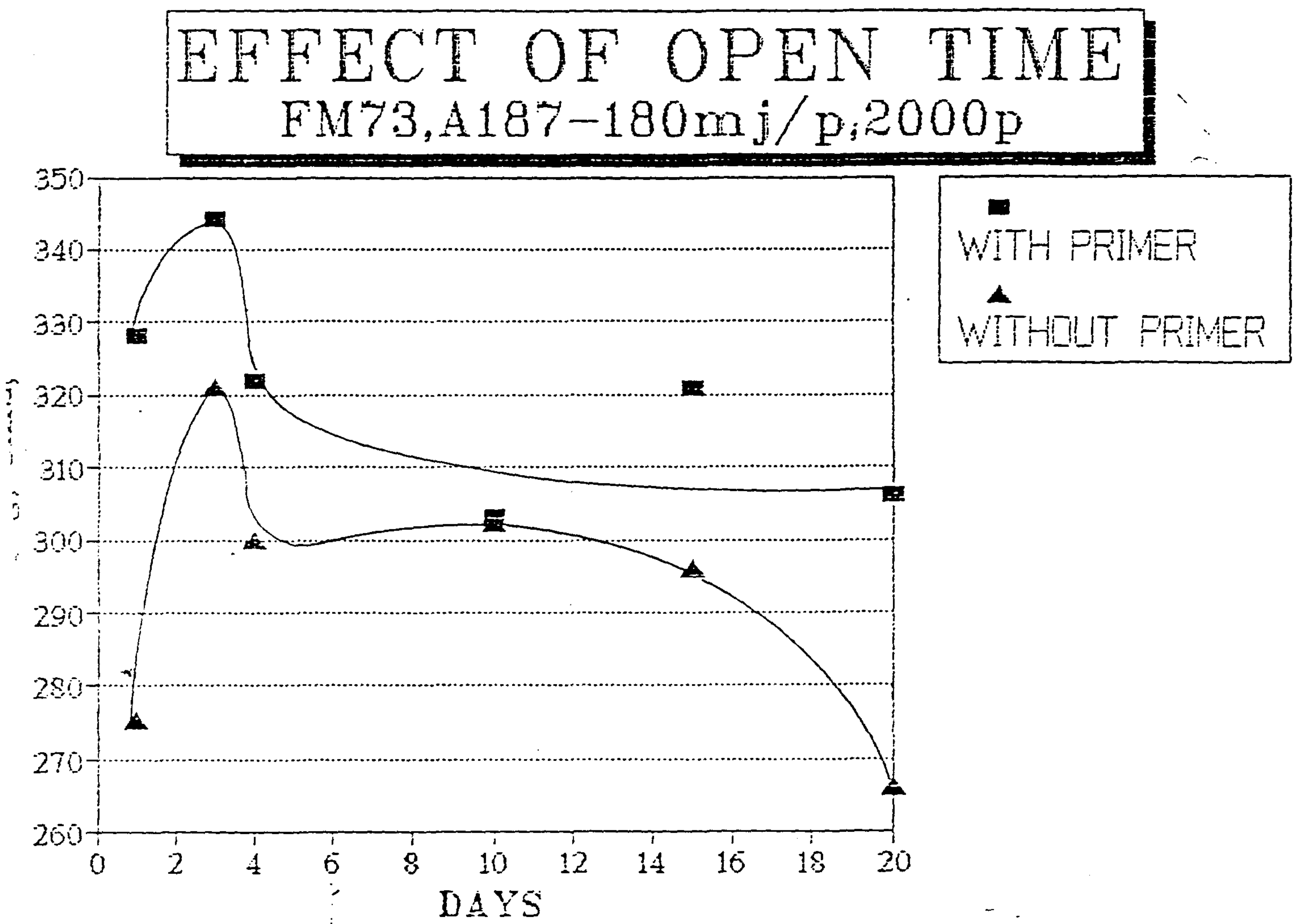


Fig. 3.3: Adhesive strength after optimal laser treatment at various periods of "open time".

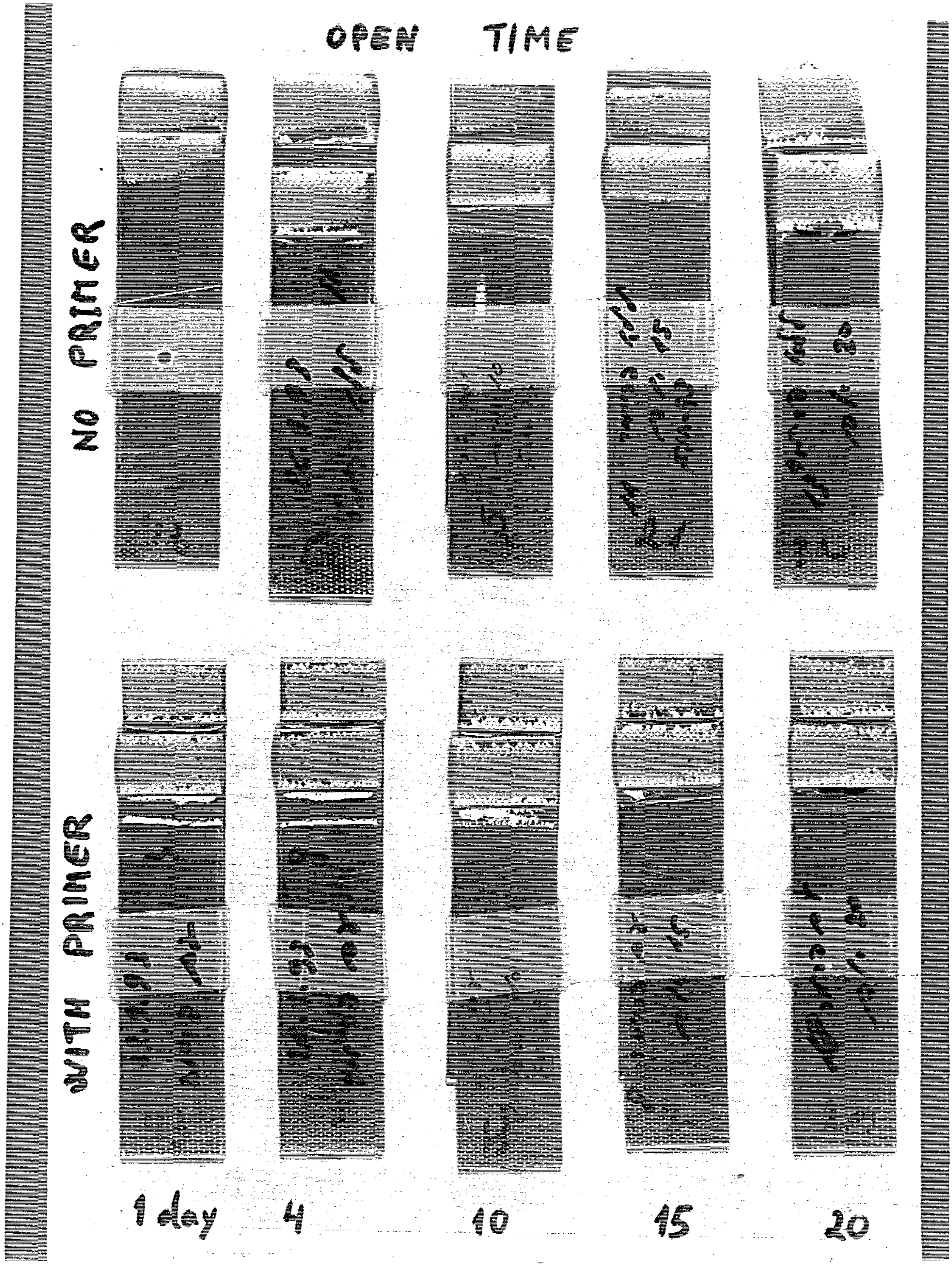


Fig. 3.4: View of laser treated joints after SLS tests -bonding after various time interval.

3.4 Tensile Tests

The FW joints were loaded in tensile mode according to ASTM C-297. Tensile adhesive strength and failure mode were determined.

The results in tables 3.2,3.3 show that laser treatment improves the tensile strengths in comparison to untreated specimen and attain values of 92%, 85% and 89% of the strength achieved with anodized treated specimens (for FM73, FM3002K and FM 350NA, respectively).

The failure mode of all the treated and non treated joints was totally cohesive for the adhesive FM73 (fig. 3.5).For the adhesive FM3002K the laser treated joints and the anodized joints failed cohesively while the untreated primed joints failed adhesively (fig. 3.5).

The failure mode of the joints bonded with FM350NA and primer BR154 was cohesive for laser treated and anodized joints and mixed for the untreated primed ones (fig. 3.6).

Table 3.2: Tensile strength(Kg/cm^2) of non treated and laser treated FW joints. Laser energy $180mj/p*cm^2$, 2000pulses and primer A187.

Surface Treatment	Adhesive	
	FM73	FM-3002K
Without treatment (primed)	369±16(c)	113±12(A)
Anodized	430±8(c)	457±17(c)
Laser treated	395±18(c)	392±16(c)

Table 3.3: Tensile strength(Kg/cm^2) of non treated and laser treated FW joints. Laser energy $180mj/p*cm^2$, 600pulses and primer BR154.

Surface Treatment	Adhesive FM350NA
Without treatment (primed)	158±31(m)
Anodized	289±21(c)
Laser treated	257±47(c)

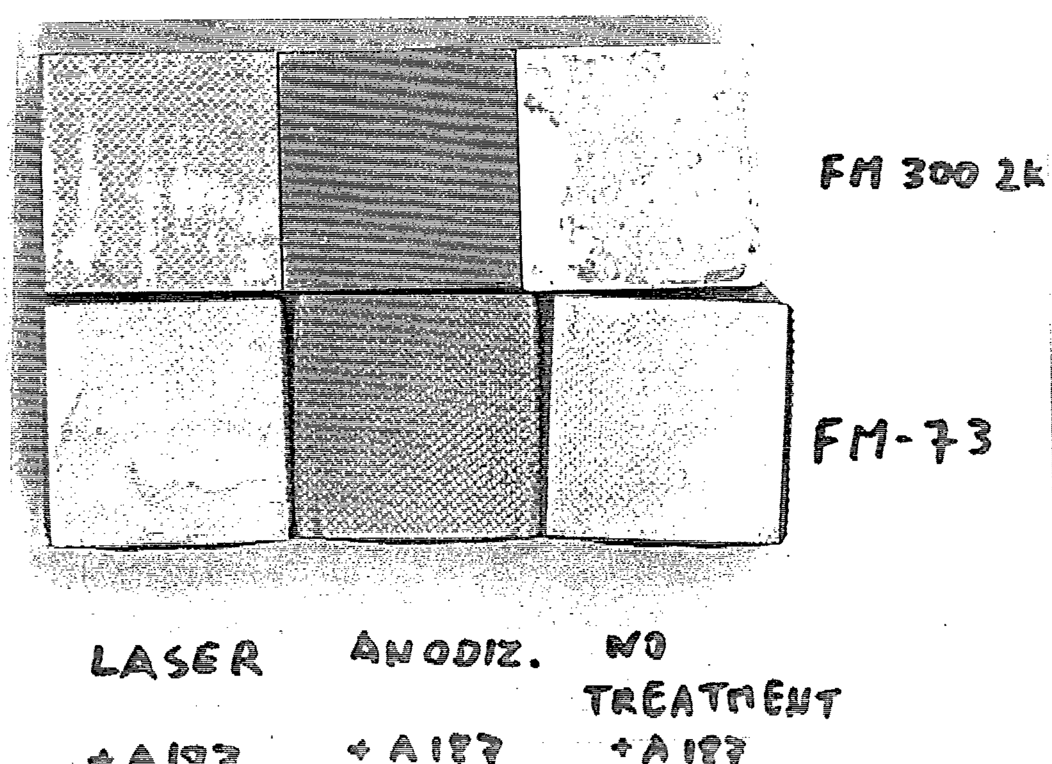


Fig. 3.5: Adherends after tensile tests.

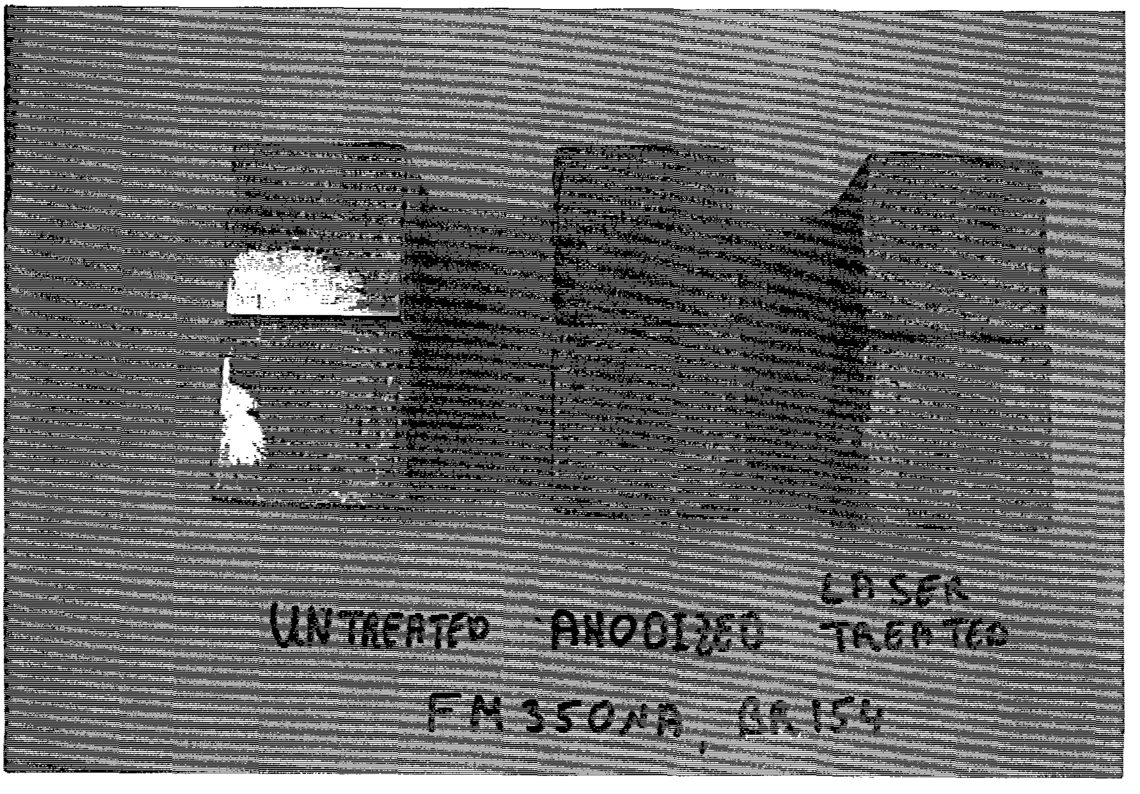


Fig. 3.6: Adherends after tensile tests.

3.5. T PEEL TESTS

Peel tests were conducted according to ASTM D-3167 (chap3.2 stage four report) peel strength and mode of failure were investigated. Tables 3.4,3.5 summarize the results of these tests.

The results in table 3.4 show that the resistance to peel of the laser treated joints was higher or similar to the anodized treated bonded with the adhesives FM73 and FM300 2K, respectively.
The resistance to peel of laser treated joints bonded with the adhesive FM350NA and the primer BR154 was 34% of the anodized specimen, but double that of the untreated one (table 3.5).

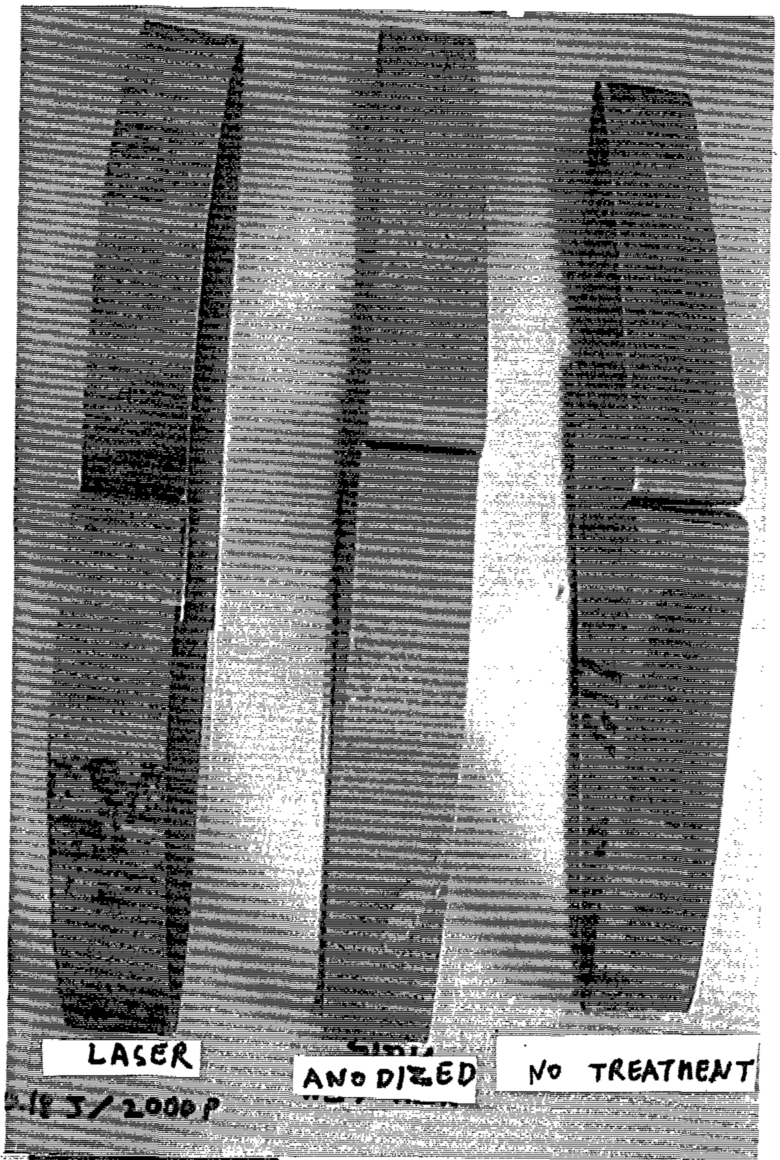
Fig.3.7 shows that the failure mode of the laser treated specimen was cohesive for FM73 and mixed for FM300 2K,as for the anodized specimen.
The laser treated joints with FM350NA and BR154 failed adhesively although the anodized joints failed cohesively.
The highest resistance to peel was achieved for FM73 and its value was ten times that of FM350NA and FM300 2K,probably due to the ductile nature of this adhesive.

Table 3.4: Resistance to peel (lib.inch) of non treated and laser treated joints (laser energy 180mj/p*cm^2 ,2000 pulses,irradiation with continuous scanning at 2.7mm/min. ,30Hz) and primer A187.

Surface Treatment	Adhesive	
	FM73	FM-3002K
Without treatment (primed)	32.9±1.4 (97%c)	2.10±1.6 (100%a)
Anodized	31.8±3.3 (100%c)	4.56±1.0 (50%c)
Laser treated	37.2±1.7 (100%c)	4.42±0.2 (60-70%c)

Table 3.5: Resistance to peel (lib.inch) of non treated and laser treated joints (laser energy 180mj/p*cm^2 ,600pulses,irradiation with continues scanning at 8.9mm/min. ,30Hz.)

Surface Treatment	Adhesive FM350 NA primer BR154)
Without treatment (primed)	0.63 (100%a)
Anodized	3.5±0.1 (100%c)
Laser treated	1.21±0.2 (100%a)



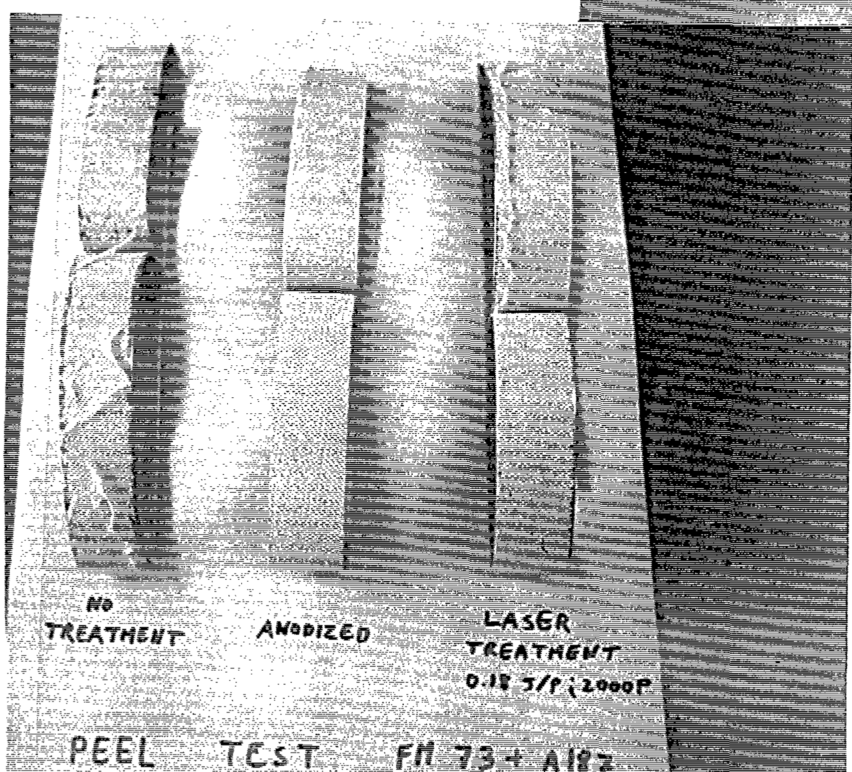


Fig. 3.7 Adherends after peel test.

3.6: Joint Resistance to Heat/Humidity

The heat/humidity resistance was tested on bonded adherends irradiated at optimal laser conditions, and primed with A187. The adhesive tested was FM73. These joints were chosen as they revealed the highest shear strength, resistance to peel and tensile strength compared with all other structural adhesives .

The results in table 3.6 show that the SLS adhesion strength of the laser treated adherends and of the anodized treated specimens did not change significantly after 10 days in humidity chamber in comparison to the untreated adherends joint which degraded by 27% of its initial strength.

The mode of failure stayed cohesive after 10 days in humidity chamber for the laser treated adherends and the anodized adherends(fig.3.8), while the untreated adhrends failed adhesively. The failure surface morphology after humidity chamber (fig.3.9) did not reveal any changes in comparison to failure morphology before exposure (fig.3.2).

Table 3.6: Shear strength of laser treated adherends after humidity chamber. Laser parameters: 180mj/p*cm², 2000pulses. Adhesive FM73, primer A187. Humidity chamber:10 days, 95%RH, 60°C.

Surface Treatment	REFERENCE S.L.S [Kg/cm²]	AFTER HUMIDITY CHAMBER S.L.S [Kg/cm²]	CHANGE IN S.L.S %
UNTREATED (PRIMED)	303±35(M/A)	220±15(M/A)	-27
ANODIZED	394±18(C)	413±6(C)	+5
LASER TREATED	344±13(C)	320±36(C)	-6

C - cohesive failure, A - adhesive failure

3.7: Shear Tests at Extreme Temperature.

The shear adhesion strengths at extreme temperatures (-30°c, +90°c) were tested on laser treated and bonded joints. The adherends were irradiated at optimal laser conditions, primed with A187 and bonded with the adhesive FM73. This adhesive revealed the highest shear strength, the highest resistance to peel and the highest tensile strength.

Table 3.7 summarizes the results ,and fig 3.8 shows the failure mode of the joints loaded in shear.

The results show a significant improvement in shear strength at low temperatures (-30°C) of the laser treated joints. The shear strength increased by 40% compared to that at room temperature. In contrast, the shear strength of the anodized bonded adherends at -30°C decreased by 16% in comparison to that at room temperature.

The failure mode at low temperatures was cohesive (fig. 3.8). Due to the extreme high shear strength of the laser treated adherends at -30°C (489Kg/cm^2) yielding of the Al adherends occurred (fig. 3.9). This phenomena was not observed with the anodized bonded joints which failed at lower shear strength (331Kg/cm^2) at -30°C.

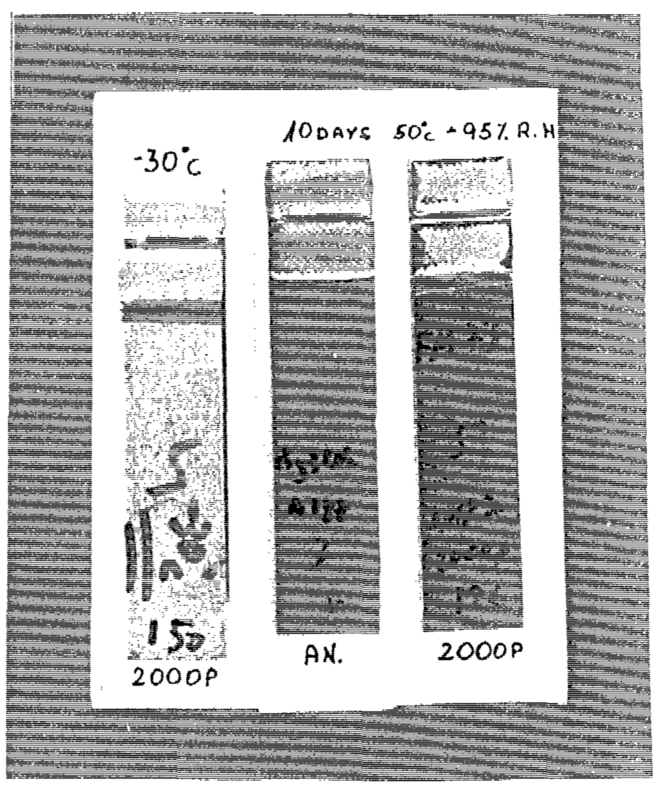
The shear strengths at +90°C of the laser treated bonded adherends and the anodized bonded adherends decreased significantly compared to the shear strengths at room temperature. The locus of the failure changed from cohesive (at RT) to interfacial adhesive/substrate at high temperature. These results indicate the limits of performance of the adhesive FM73 with the primer A187 at this temperature (+90°C). Although the values of the shear strengths reduced to 100Kg/cm^2, it is still adequate to the requirements for structural bonding.

Table 3.7: Shear strength at extreme temperatures of laser treated bonded joints. Laser parameters: 180mj/p*cm², 2000pulses. Adhesive FM73, primer A187.

Surface Treatment	R.T S.L.S Kg/cm²	-30°C S.L.S Kg/cm²	+90°C S.L.S Kg/cm²
ANODIZED	394±18(C)	331±40(C)	183±7(A)
LASER TREATED	344±13(C)	489±10(C) Al yielding	105±7(A)
UNTREATED	303±6(A)	---	72±14(A)

C- cohesive failure

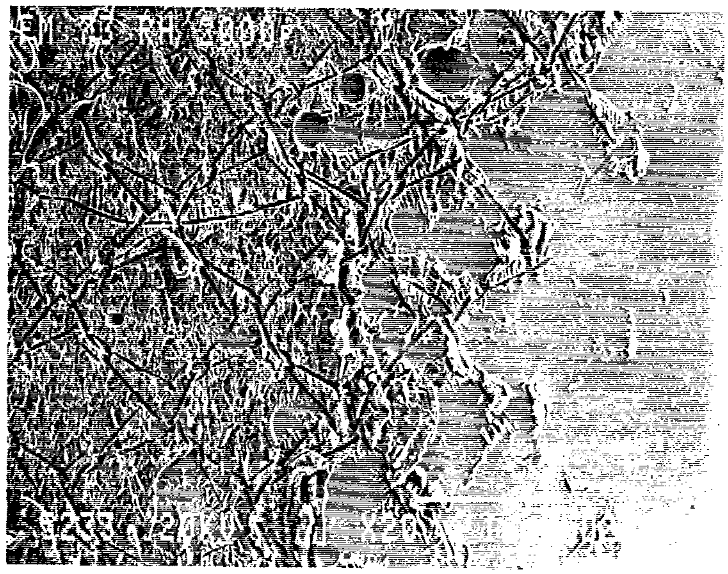
A- adhesive failure



A B

Fig. 3.8: Shear failure surface: A) after 10 days in humidity chamber (95%RH,50°C),and B) after testing at -30°c. Adhesive FM73, primer A187.

General view



Adherence of the
adhesive to the substrate

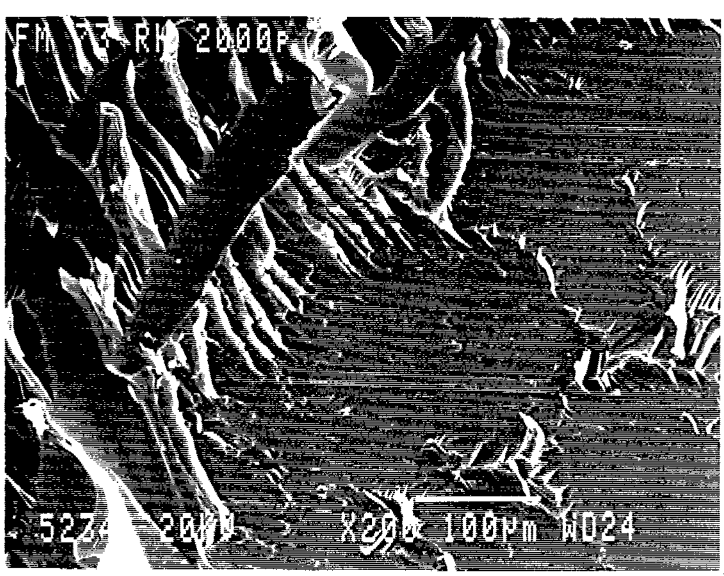


Fig. 3.9: SEM micrographs of the surface failure morphology of SLS joints after 10 days in humidity chamber. Adhesive FM73, primer A187. Laser energy 180mj/p*cm², 2000pulses).

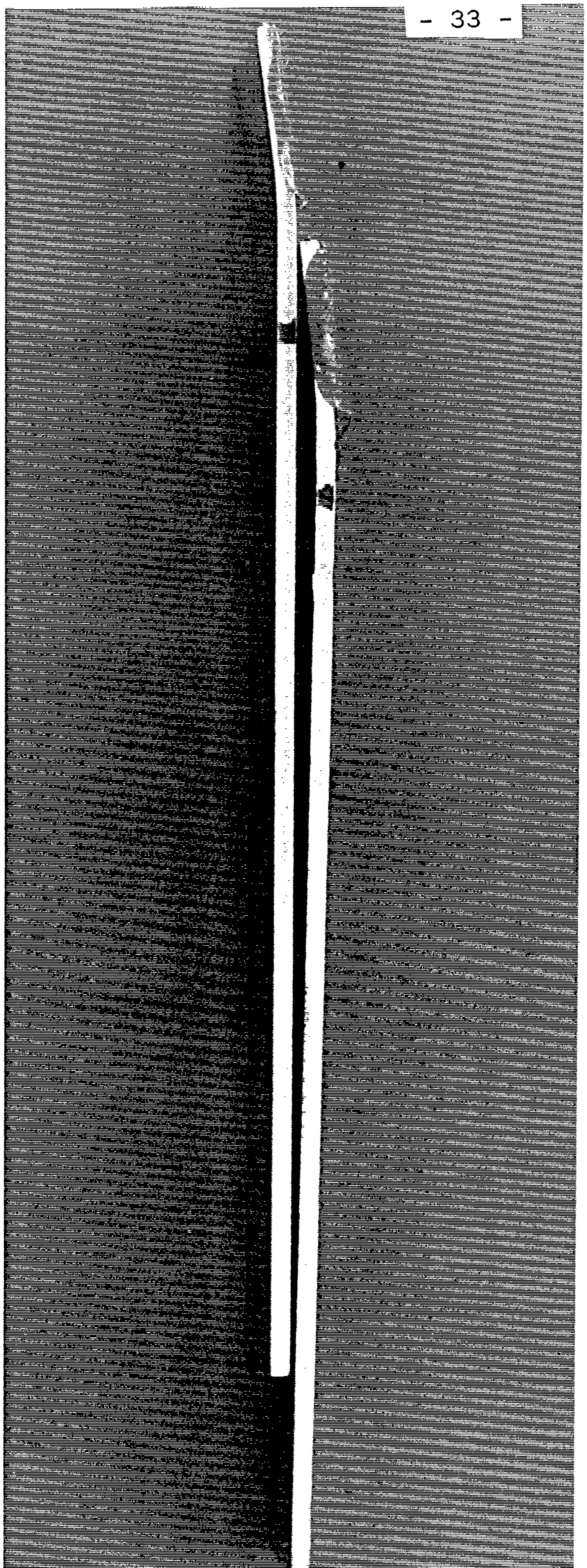


Fig.3.10: Visual observation of laser treated adherends after SLS test at low temperature.

3.8: Durability Wedge tests

The results of the crack length as function of exposure time for the durability wedge joints bonded with the three structural adhesives are summarized in fig 3.11. In each figure these different surface treatments are presented: No treatment, anodization and laser treatment.
The joints, after exposure were forced open and their surface texture is shown shown in fig.3.12.
The laser treated adherends were irradiated at the optimal laser conditions (table 3.1) and treated with the primer A187 directly after irradiation.
The results in fig.3.11 show that the untreated adherends failed totally (crack length = wedge length) after 4hrs. exposure for all three structural adhesives.
Laser treatment and anodization caused the crack to stop from advancing after 70% and 50% of the wedge length respectively.
FM73 performed the best durability as the crack stopped and was stable after 60% and 40% of the wedge length.
For all three adhesives the durability of the laser treated joints is better than for untreated adherends but some less than the anodized ones.

Fig. 3.12a shows that joints bonded with the adhesive FM73 opened cohesively in the initial stage and than the crack progressed adhesively\mixed for the laser treated and the anodized joints and totally adhesive for the untreated joints. At the end of the test, the joints were opened cohesively by force.
Fig. 3.12b shows that the laser treated and the anodized joints with the adhesive FM3002K opened cohesively at the initial stage while the untreated joints opened adhesively. The crack progressed adhesively during the exposure period, for all the joints. When opened by force at the end of the tests the anodized and the laser treated joints failed cohesively while the untreated joints failed adhesively.
A similar effect can be seen in joints with FM350NA except the fact that the failure is adhesive and divided between the two adherends (Fig.3.12c).

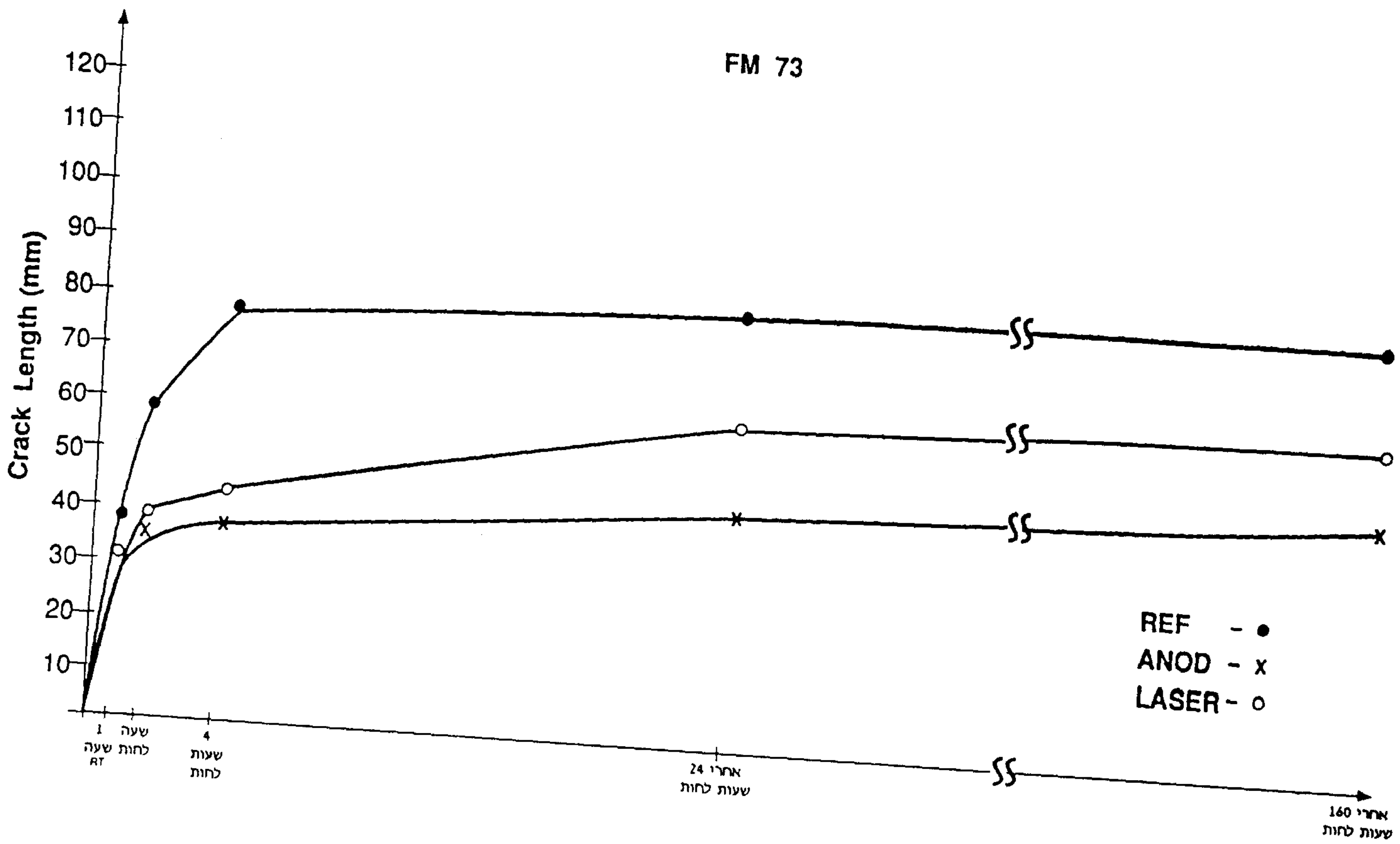


Fig 3.11: Summary of results of wedge tests with three adhesives.a: FM73.

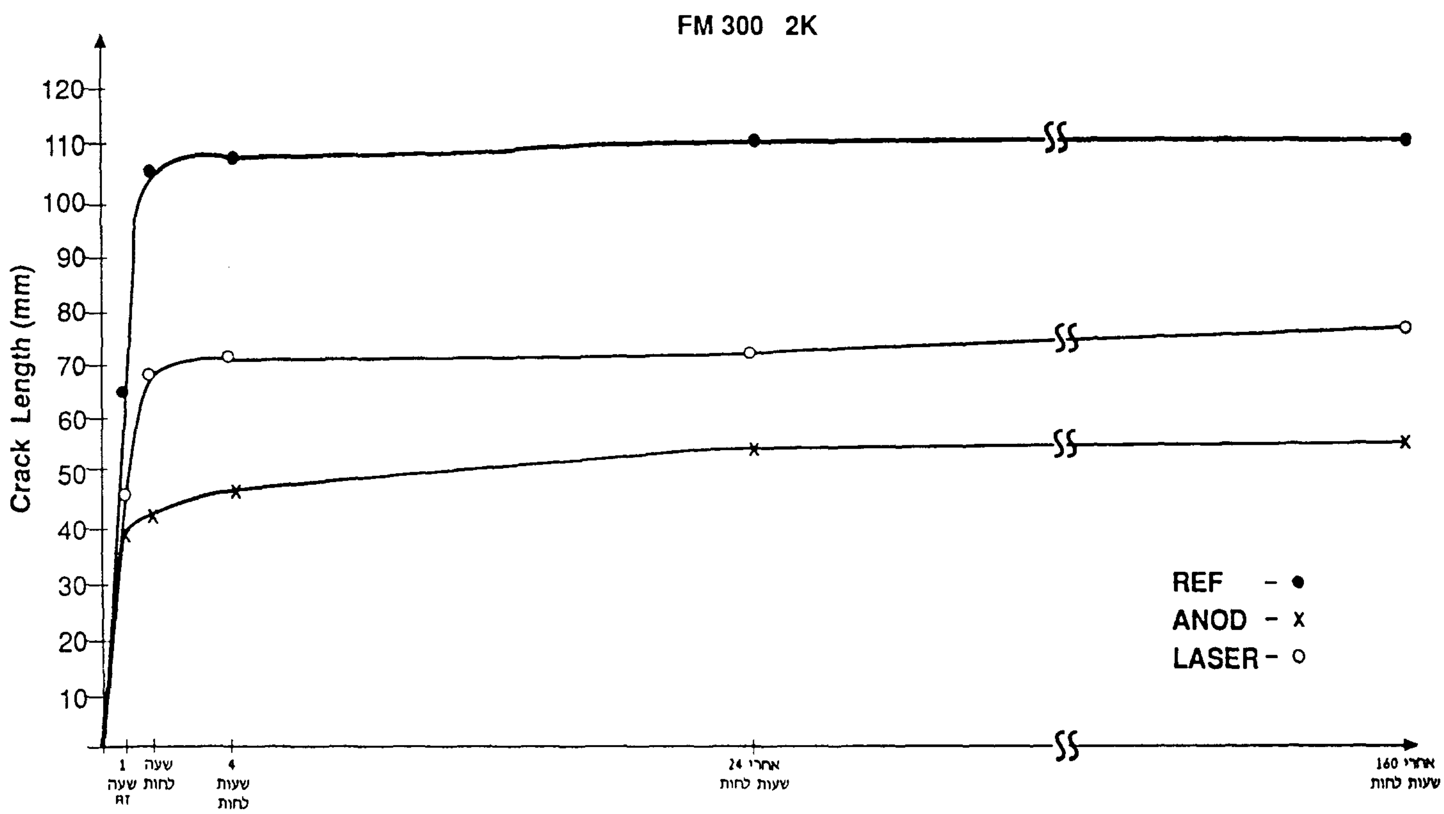


Fig 3.11: Summary of results of wedge tests with three adhesives.B: FM300 2K.

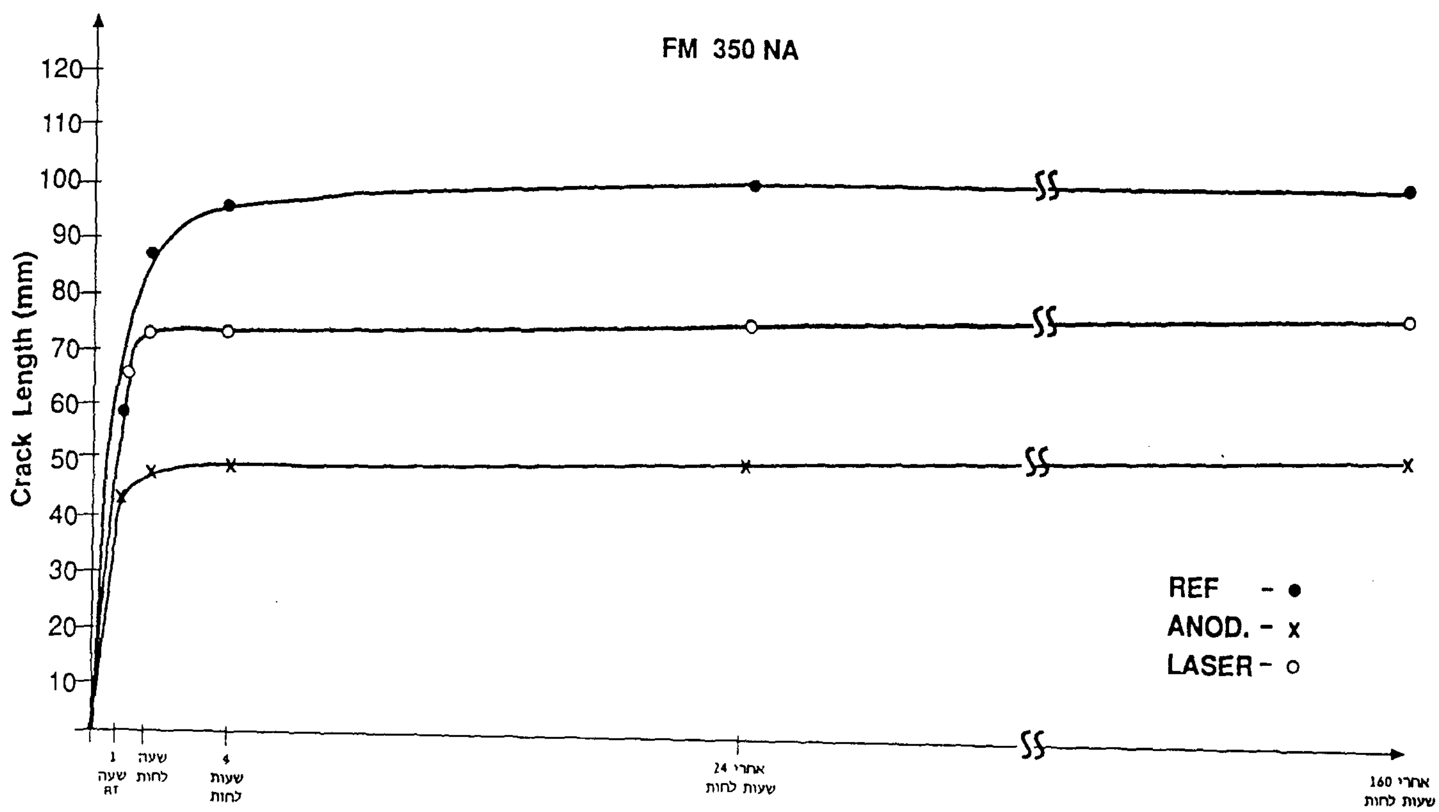


Fig 3.11: Summary of results of wedge tests with three adhesives.C: FM350 NA.

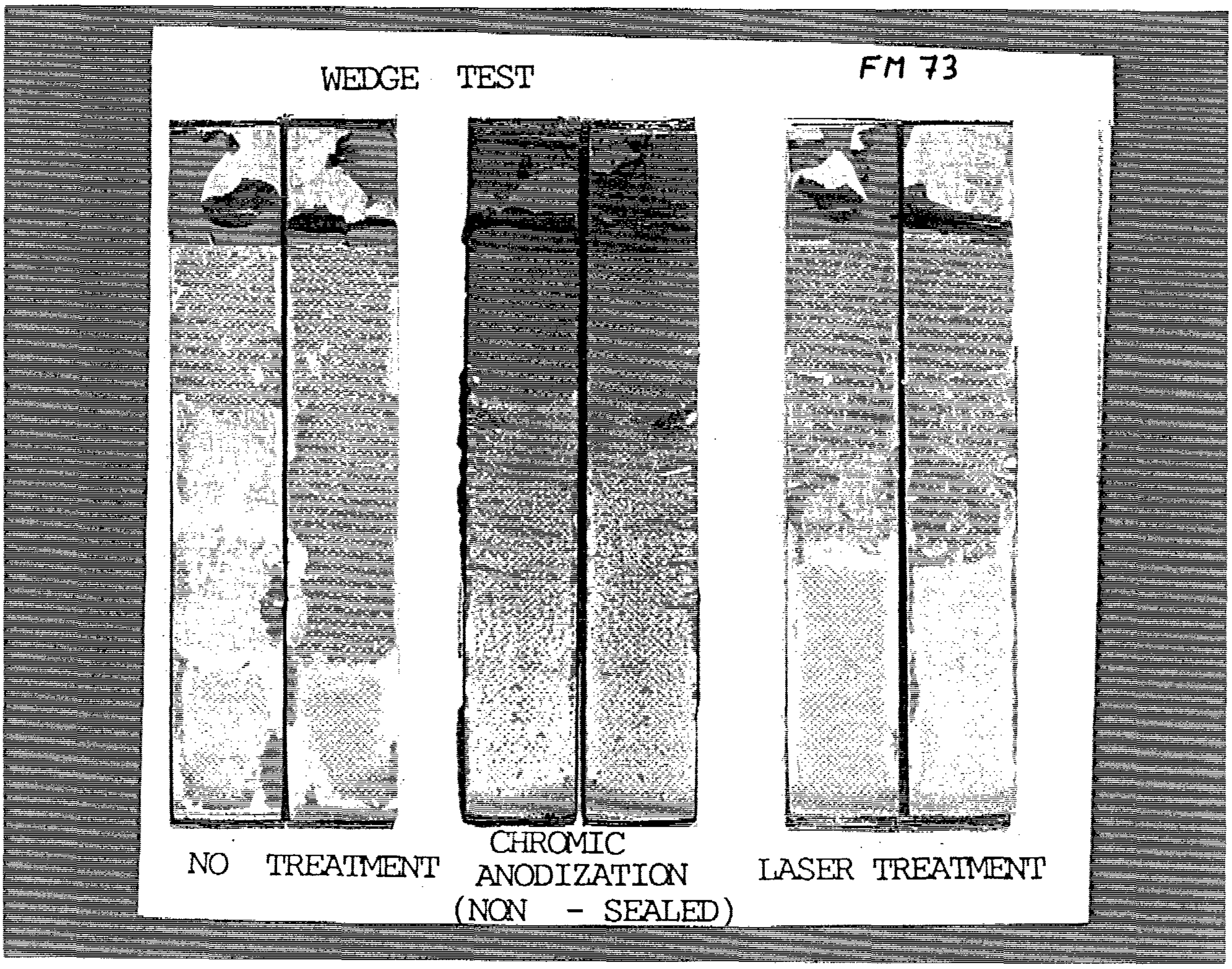


Fig.3.12: General view of the opened adherends after wedge tests. a:with the adhesive FM73.

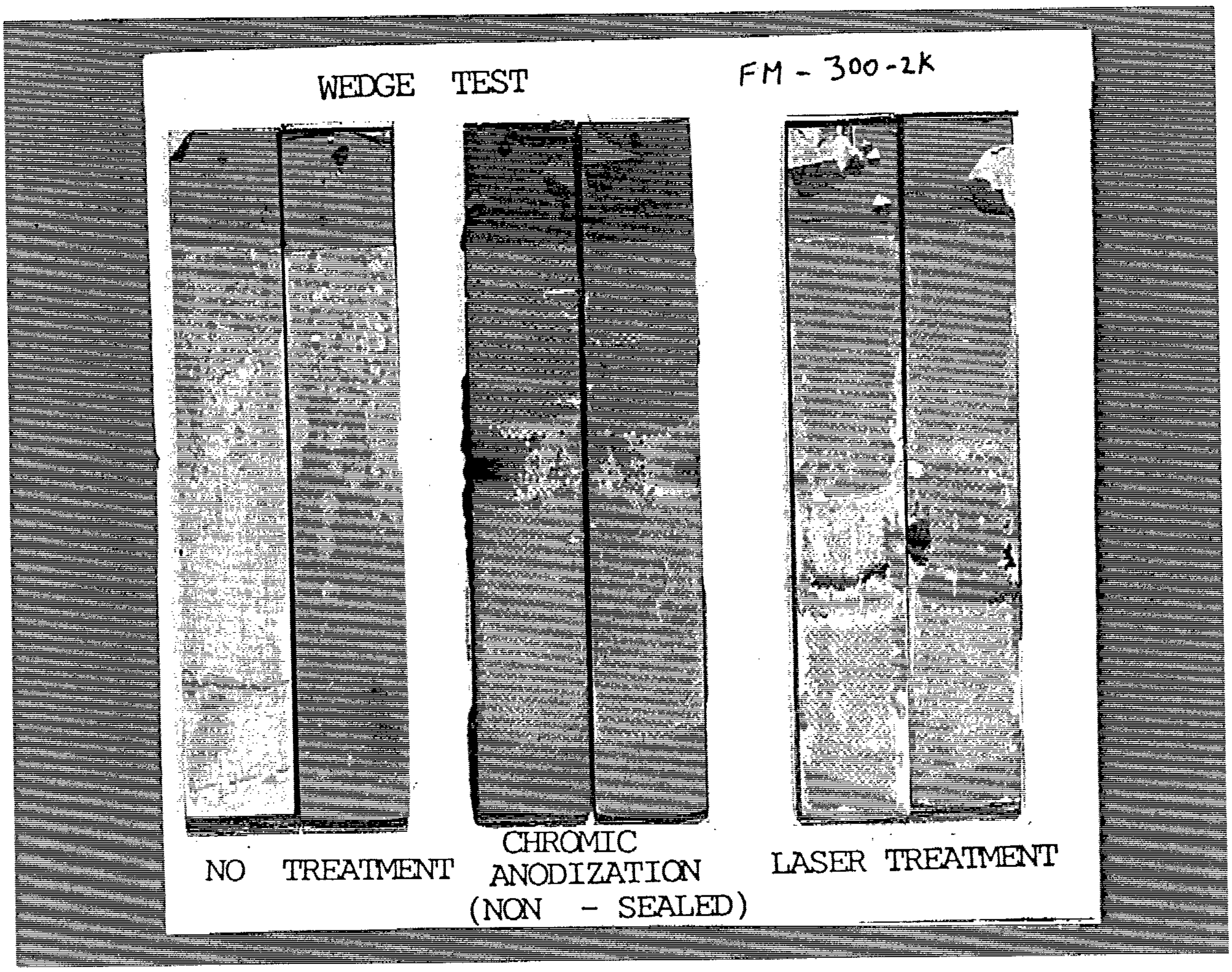


Fig.3.12: General view of the opened adherends after wedge tests. b:with the adhesive FM300 2K.

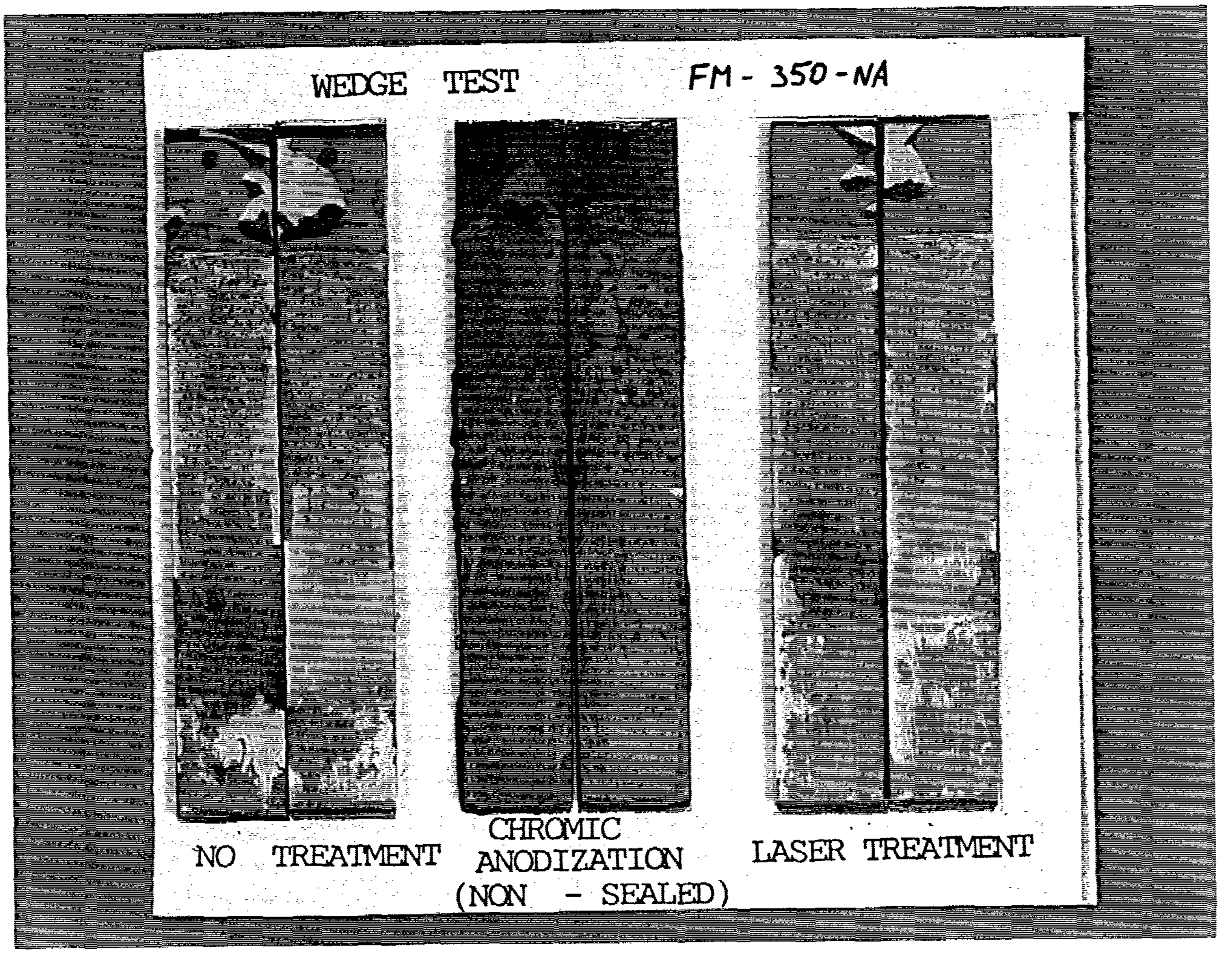


Fig.3.12: General view of the opened adherends after wedge tests. c:with the adhesive FM350 NA.

3.9: Effect of Laser parameters on Al Surface morphology (before bonding).

Aluminum samples irradiated at various laser conditions were examined by SEM in order to study the effect of laser energy and number of pulses on the surface morphology. Auger, FTIR and contact angle measurement analysis were also conducted to complete the information and gain better understanding.
The various analysis results indicate that various mechanisms are involved in the laser treatment at different laser parameters (energy and time of irradiation).

3.9.1: SEM and AUGER analysis

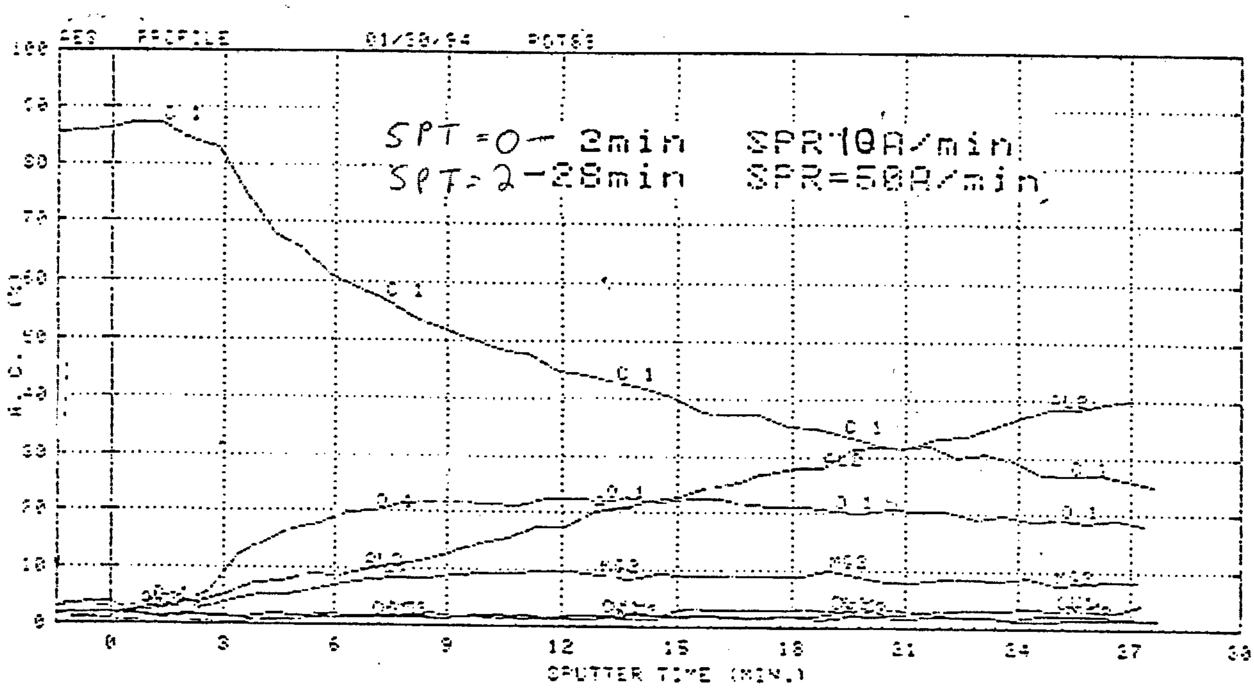
Irradiation at $0.18J/p*cm^2$ did not produce any morphological changes on the surface, although cleaning and oxides layer formation was observed, at this energy level, by Auger and FTIR spectroscopy (1,4) (fig 3.13b) (chaps.3.2, 3.3 stage 3 report).

At higher laser energy of $0.57J/p*cm^2$ surface texture smoothing after 50 pulses irradiation , and formation of cracks and material removal after 1000pulses were observed (fig. 3.8 stage four report). The oxide layer formed at this energy was thicker (about 900A) than that produced at laser energy of $0.18J/p*cm^2$ (fig 3.13c) (figs 3.20 stage 3 report).

Irradiation of Al specimen by laser energy of $1J/p*cm^2$ with 10 and 100 pulses caused surface smoothing, disappearing of the machining lines and evaporation of intermetallic particles forming small holes at the surface. Irradiation of 100 pulses resulted, in addition in formation of fine ripples on the surface (fig 3.13d)(fig. 3.9 stage four report).

Auger profiles (fig.3.20 stage 3 report) indicate that irradiation with 10 pulses at $1J/p*cm^2$ resulted in formation of oxide layers of Al and Mg.The oxide thickness is about 700°A, thinner than that produced at lower energies, probably due to ablation at high energy. Irradiation with 100 pulses (fig 3.13d) resulted in formation of aluminum oxide layer (without Mg which is less stable). The ratio of Al oxygen in this layer corresponds to Al_2O_3 ,i.e. O: 60% and Al: 30%. The oxide layer thickness after 100 pulses was about 600°A.

Irradiation with energy level of $2.7J/p*cm^2$ results in the disappearance of the surface machining lines and creation of a rougher surface than that obtained at lower energies. Irradiation with 10 and 50 pulses (fig.3.13e) results in a wavy morphology with embedded particles. Increasing the number of pulses to 100 results in smoother morphology with protruded ripples and holes originating from particle evaporation.
Auger depth profiles indicates that the combined reaction of ablation and melting results in introduction of nitrogen into the upper surface layer(Al nitration). This layer of oxide -nitrogen aluminum is very thin (≤150°A) (fig.3.13e) (fig. 3.22 stage 3 report).



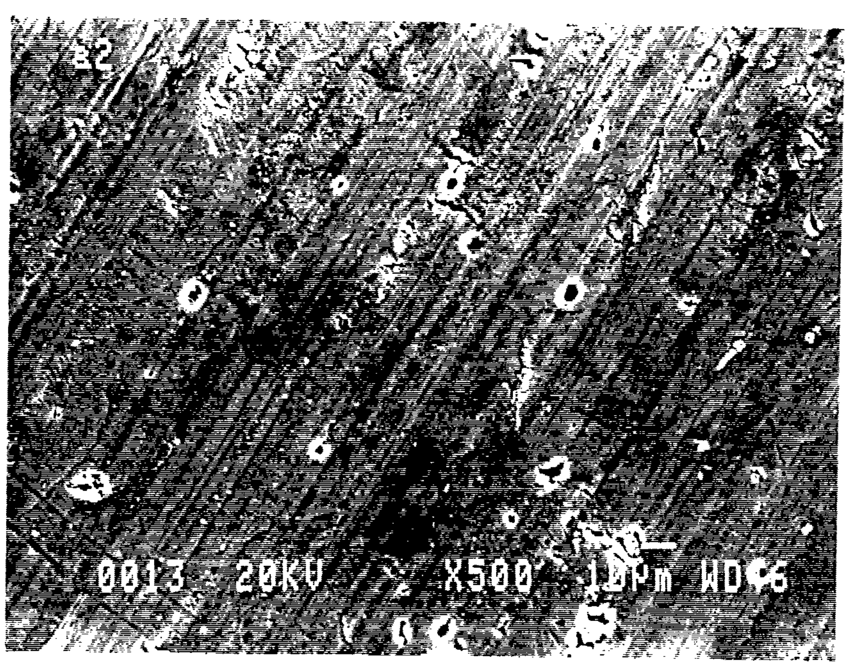


Fig. 3.13a: Auger depth profile and SEM micrograph of untreated Al surface.

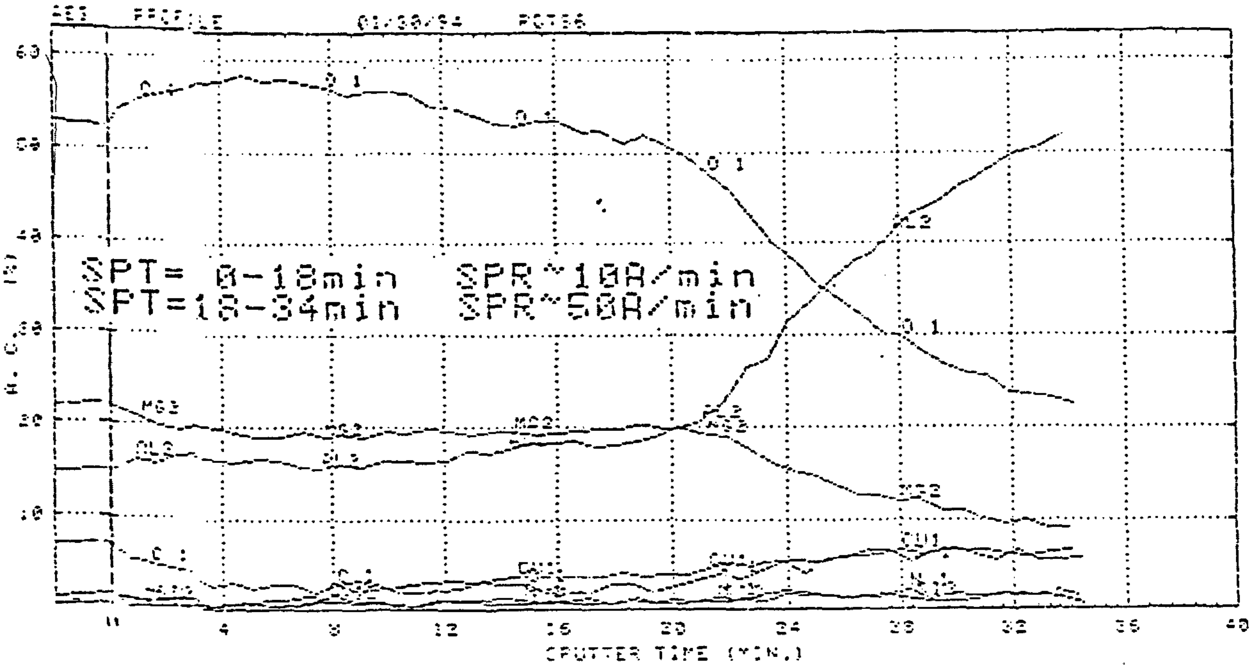


Fig.:3.13b: Auger depth profile and SEM micrograph of laser treated Al surface: laser energy 180mj/p*cm² ,2000pulses.

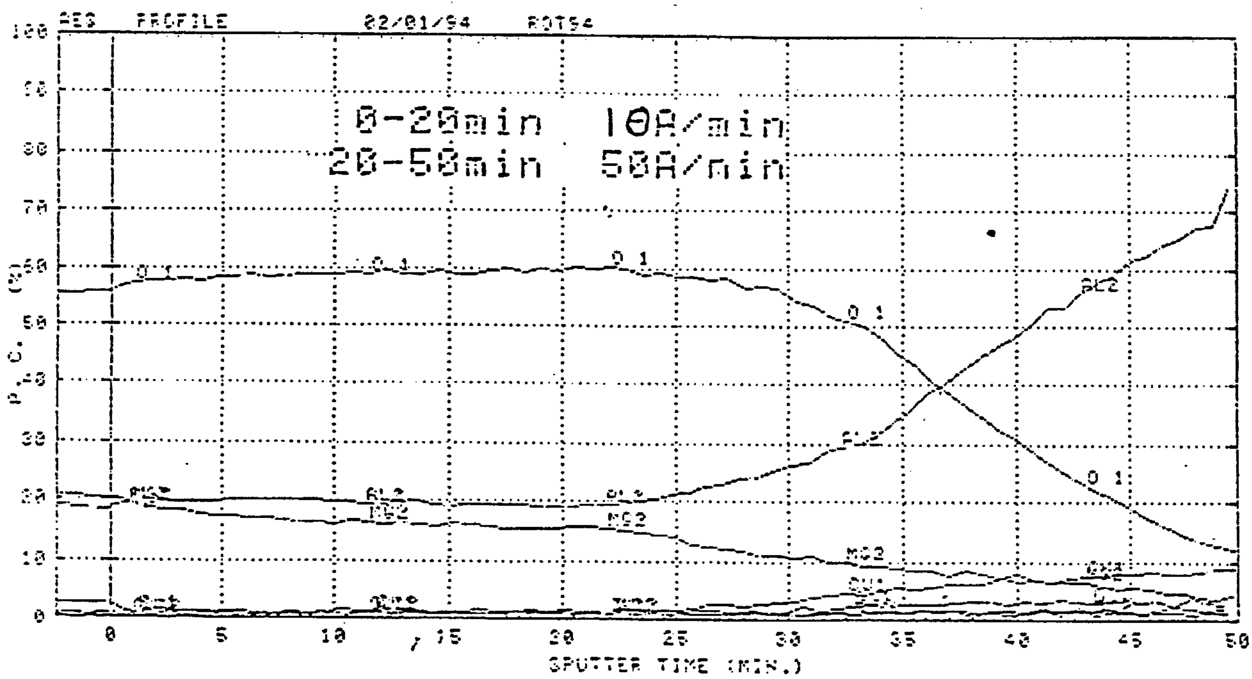
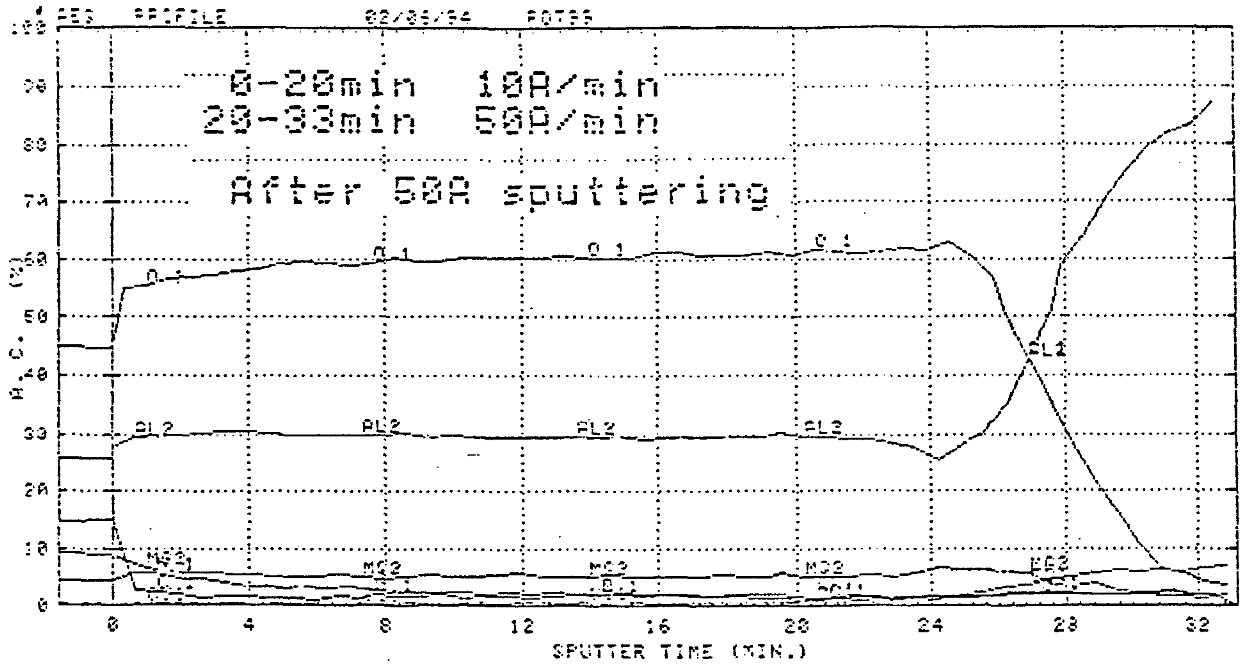


Fig.:3.13c: Auger depth profile and SEM micrograph of laser treated Al surface: laser energy 0.57J/p*cm²
,1000pulses.



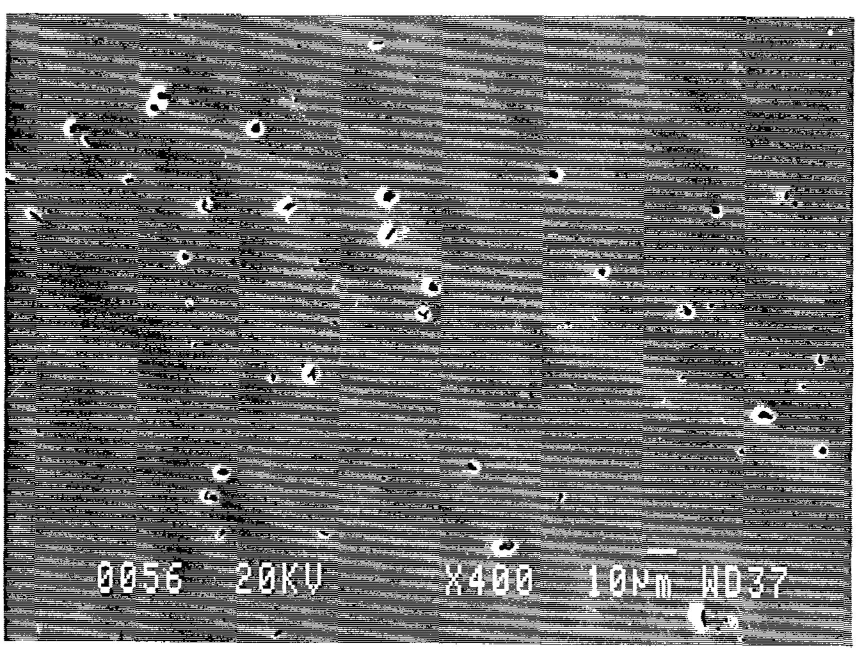
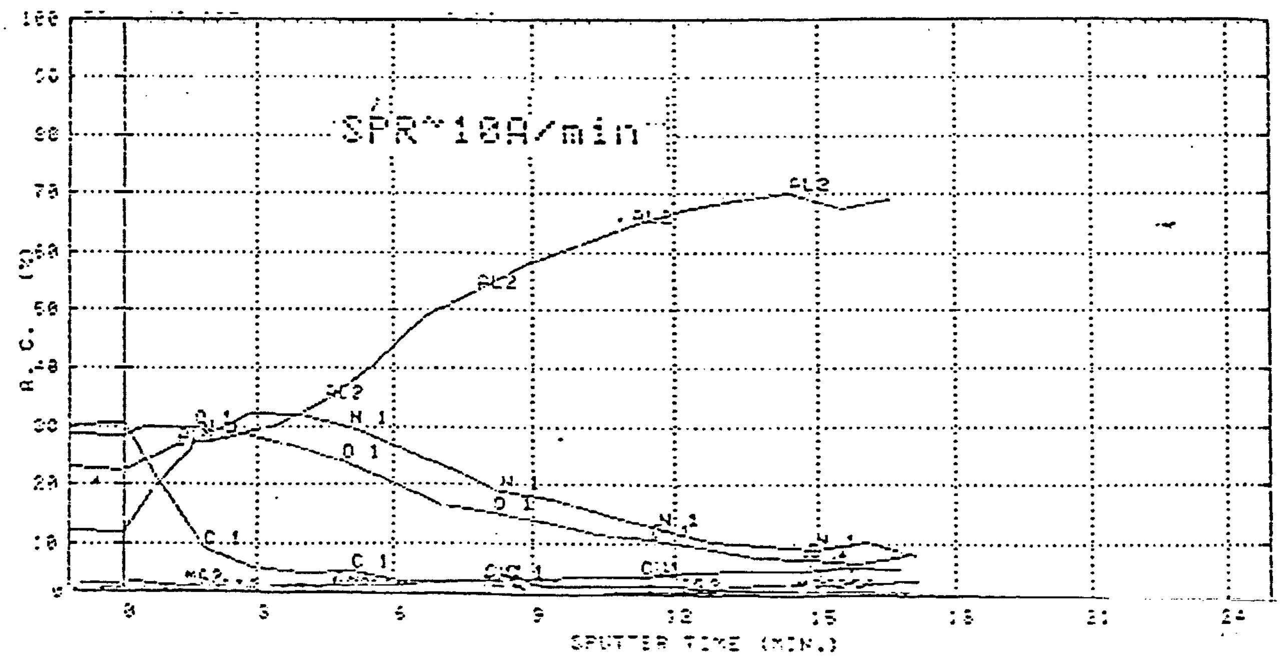


Fig.:3.13d: Auger depth profile and SEM micrograph of laser treated Al surface: laser energy 1J/p*cm^2 ,100pulses.



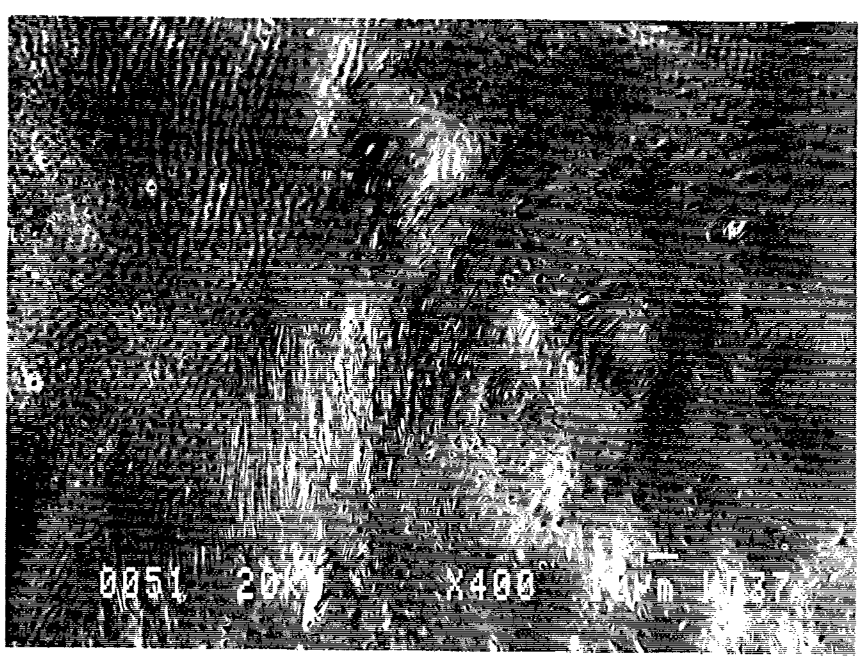


Fig.:3.13e: Auger depth profile and SEM micrograph of laser treated Al surface: laser energy 2.7J/p*cm² ,50pulses.

3.9.2: Contact angle measurements

The strength and durability of an adhesion joint depends on the ability of wetting the surface of Al adherend by the adhesive. The common way to determine the surface activity is by measuring the contact angle (Θ). A drop of liquid is placed on the adherend and contact angle is measured at the point where the two phases meet (solid/liquid). Perfect wetting occurs when $\cos\theta=1$ ($\theta=0$). Lower θ indicates better wetting. Surface treatment can improve wetting by increasing surface energy and lowering Θ.
Contact angles of treated and untreated Al adherends were measured with water drops using a Contact Angle indicator .

Results show that laser treatment caused significant decrease in the contact angle compared to untreated Al, which indicates improved wetting. Table 3.8 summarizes these results. The lowest contact angle was found for laser energy $0.18 J/p*cm^2$ which also resulted in the maximal adhesion shear strength. Higher energies cause surface smoothing which results in higher Θ.

Table 3.8: Effect of laser treatment on contact angle between water and laser treated aluminum.

Sample	Laser energy $J/p \cdot cm^2$	Pulses No.	Contact angle, 0°
Untreated	-	-	90
Laser treated	0.18	100	58
		600	52
		1000	43
		2000	41.6
		5000	43
	1	1	56
		10	59
		100	52
	4	1	51
		10	62

3.9.3: Infra-Red spectroscopy

Figs. 3.14 -3.15 present FTIR spectra of laser treated aluminum adherend. The adherends were cleaned by a degreasing process before laser irradiation. The irradiation was carried out in air with and without oxygen.
Fig.3.14 is the spectra of the irradiated adherends ($400cm^{-1}$ - $4000cm^{-1}$) and fig.3.15 is an enlargement of the spectra in

the range of $400cm^{-1}$ -$2000cm^{-1}$. The main absorbance peaks appearing in these figs. are:

1. $3200cm^{-1}$ AlO-H +H_2O (stretch) (5,6)
2. $1600cm^{-1}$ AlO-H_2O (stretch) absorbed water molecules(5,6)
3. $1450cm^{-1}$ Al-O (stretch) (5,6)
4. $1119cm^{-1}$, $1100cm^{-1}$
5. $1072cm^{-1}$
6. $950cm^{-1}$
7. $792cm^{-1}$
8. $612cm^{-1}$
9. $520cm^{-1}$
10. $460cm^{-1}$

The peaks at the wavelength range of $400\text{-}1100cm^{-1}$ belong to various hydroxides (7,8) as described in figs. 3.16, 3.17.
The spectrum of the specimen irradiated in air oxygen atmosphere differ from those irradiated without an oxygen stream (figs. 3.14,.3.15).
Comparison between fig. 3.15a and fig. 3.15b show more defined peaks at $1600cm^{-1}$,$1450cm^{-1}$,$1416cm^{-1}$ and $1362cm^{-1}$ for the spectrum of the specimen irradiated without oxygen.
These results prove the assumption that the oxygen probably reacts with the active sites created on the surface by the laser irradiation reducing their concentration and the chemical activity of the surface .
A new peak at $660cm^{-1}$ appears under oxygen atmosphere typical to an oxygen rich hydroxide (AlOOH).

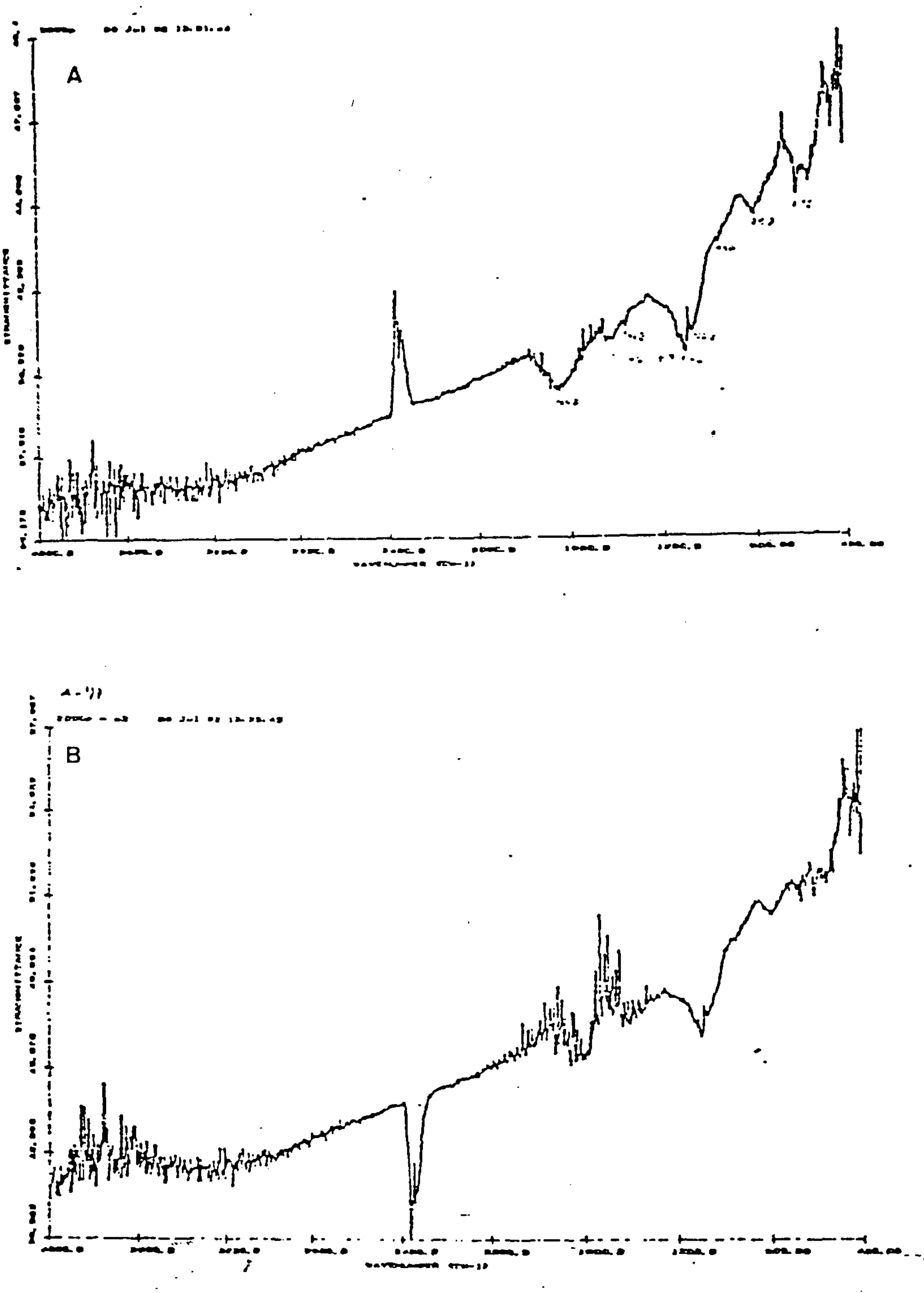


Fig.3.14: FTIR spectra of irradiated aluminum.Laser energy 0.18j/p*cm², 2000 pulses. a. without oxygen stream. b. with oxygen steam.

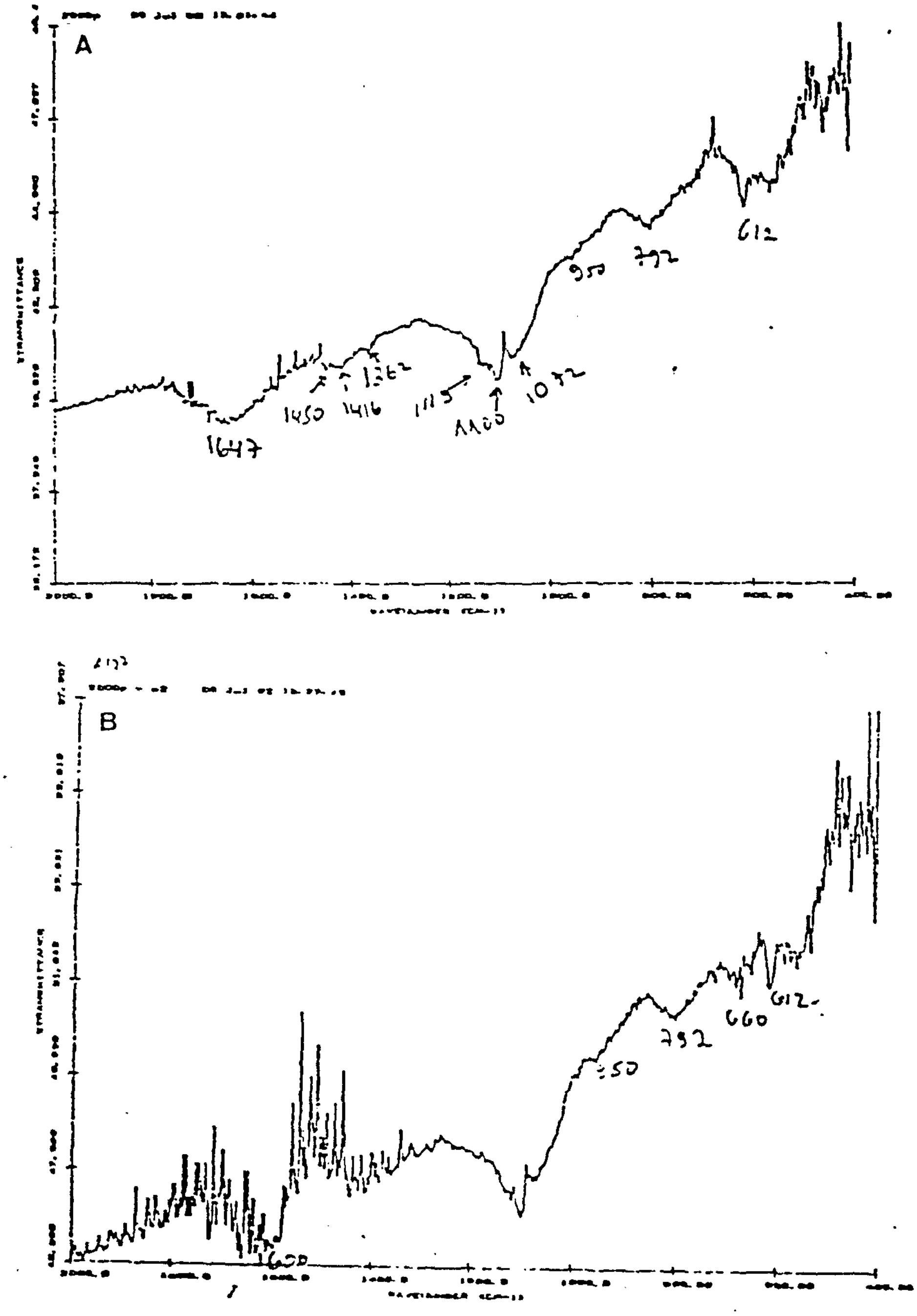


Fig. 3.15: Enlargement of FTIR spectra of fig.3.14 at the wavelength range of 2000-400cm^{-1}. a. without oxygen stream. b. with oxygen stream.

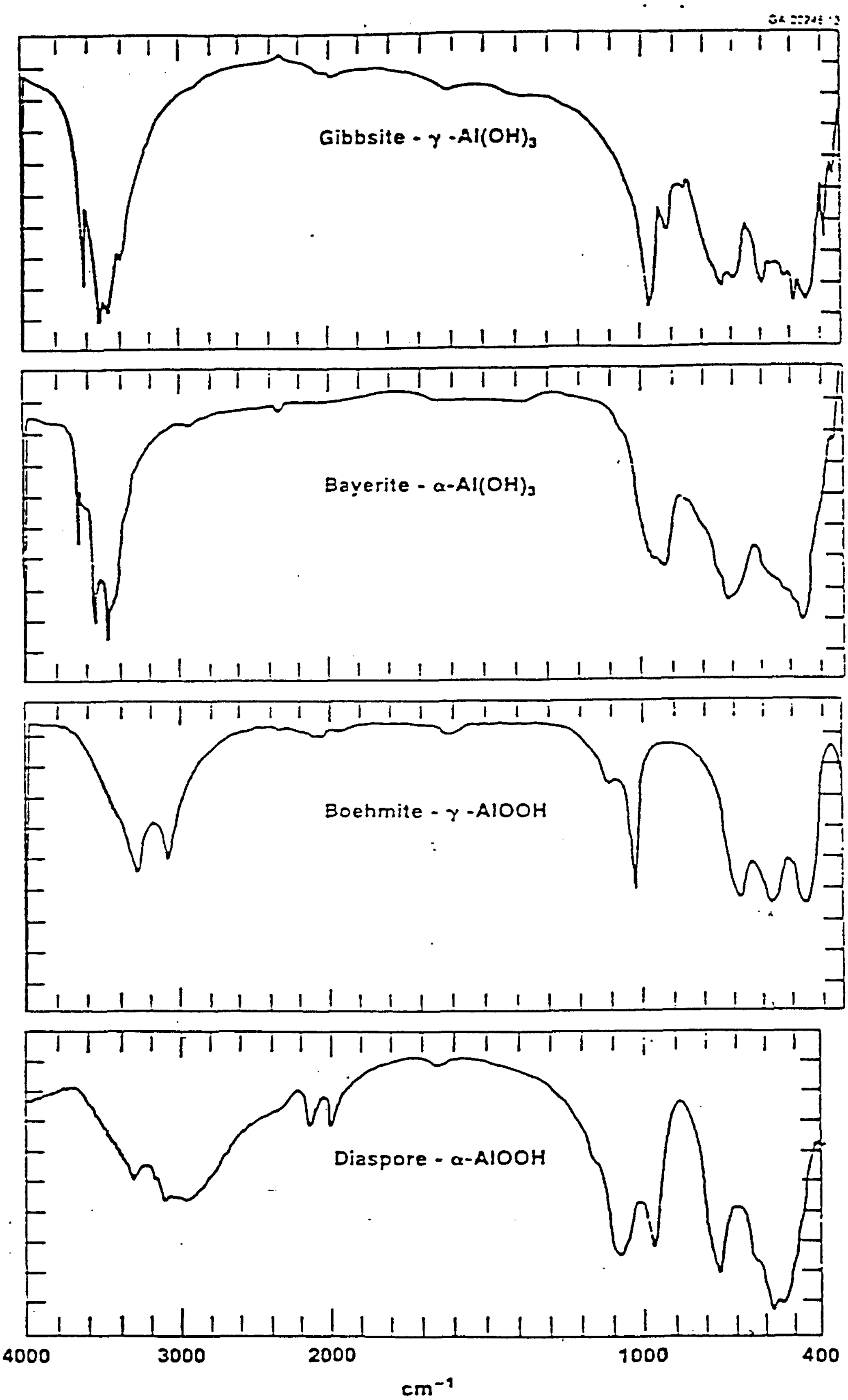


Fig.3.16: Infra Red specta of various aluminum hydroxide(7).

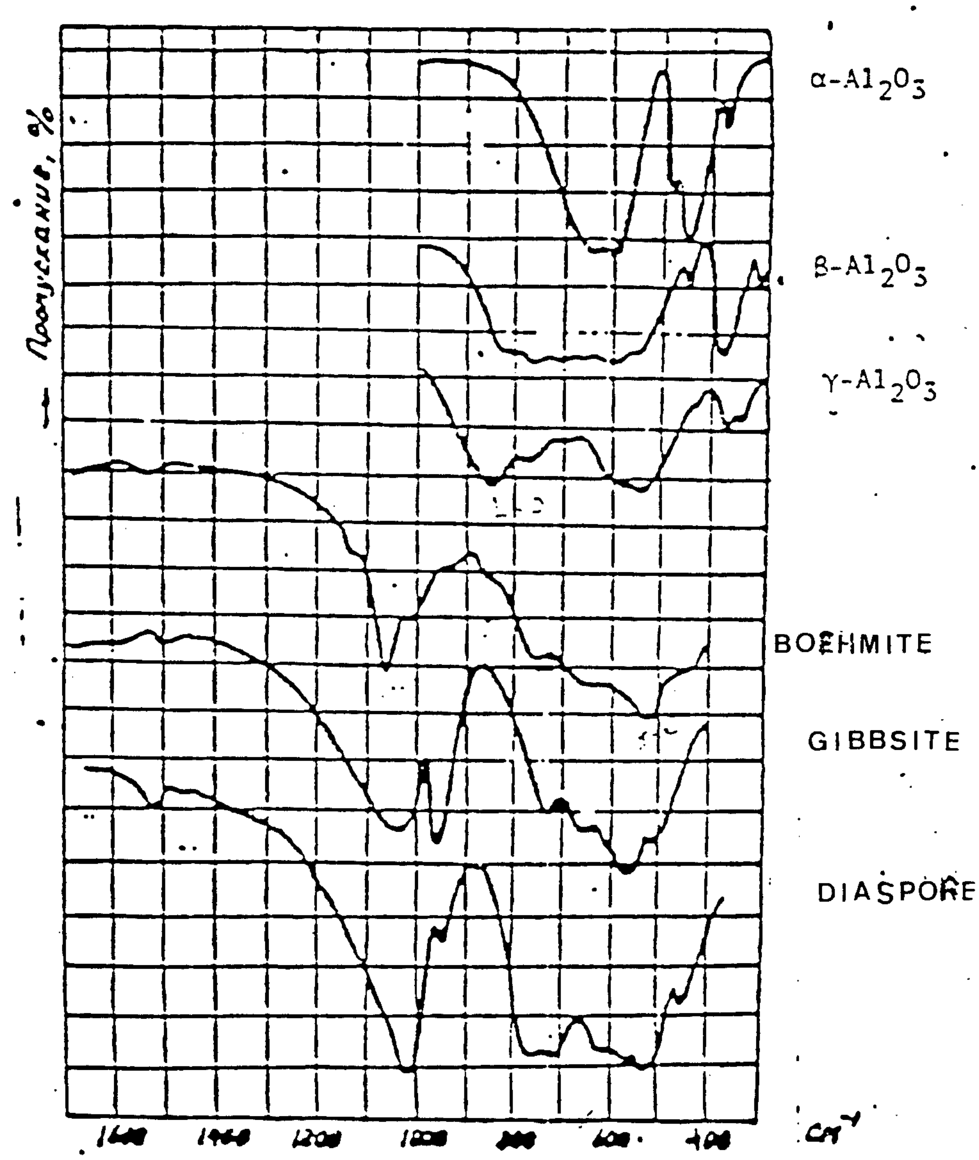


Fig.3.17: Infra Red spectra of aluminum oxides and hydroxides (8).

The above results show that different processes occur at various laser energies and time of irradiation: At low laser energy $0.18J/p*cm^2$ ablation of organic contaminants and oxidation of Al and Mg occurs without morphological changes due to mostly photochemical ablation and photo-oxidation reactions. These results shear the lowest contact angle and better adhesion strength.

An increase in energy density causes changes in surface morphology. At $1J/p*cm^2$ the laser energy density was high enough to produce surface smoothening through thermal ablation with oxide formation and contact angle decreasing. Higher laser energy ($2.7J/p*cm^2$) resulted in massive plasma formation and an increased surface roughness. This roughness resulted from an explosively spreaded plasma cloud that freezes on the surface in rapid solidification. The plasma wave moves from the middle to the rims as can be seen in fig.3.12 stage four report. Plasma formation causes additional reactions such as participation and nitridation.

4. SUMMARY AND CONCLUSIONS

The potential of UV lasers irradiation as prebonding treatment of Al-2024 alloy was proved in a previous investigation(1) using a modified epoxy adhesive(2).
In this research a similar treatment was tested but on Al joints with structural adhesives which are normally used in bonding and repairing processes for aerospace application. In order to achieve high adhesive strength optimal laser parameters for the treatment were chosen. Various mechanical tests were conducted in order to evaluate this technique including: peel, shear and tensile tests, and durability studies.

Results showed that laser treatment of Al adherends with optimal laser parameters and priming with a silane water base primer A187 resulted in better adhesion strength than non treated primed joints. Adhesion strength was close to that obtained with anodization +primer .

Adhesion shear strength (SLS tests) with laser treated adherends improved by more than 150% compared to untreated Al adherends, and was 85-97% of the shear strength of the chromic acid anodized Al adherends bonded with the adhesives FM73,FM300 2K and FM350NA. The highest values that were achieved were 344Kg/cm^2 with FM73, 294Kg/cm^2 with FM300 2K, and 217Kg/cm^2 for FM350NA compared to anodized adherends (394Kg/cm^2, 306Kg/cm^2 and249Kg/cm^2, respectively).

Application of the primer BR127 did not improve the shear strength probably due to etching of the fine morphology created by the laser treatment on the surface of the adherend. In the other side silane A187 was suitable as a primer following laser irradiation for the three adhesives(FM73, FM300 2K and FM350NA).

Other advantages of A187 are: better homogeneity, thin layer application and a water base primer (no etching of anodization).

Open time studies showed that adhesive bonding can be applied even 20 days after laser treatment providing that primer was applied immediately after laser irradiation.

The preferred laser treatment for Al2024 adherend are: $0.18j/p*cm^2$ with 1000 to 2000 pulses at a repetition rate of 30Hz.

For all the adhesive tested, failure mode after laser treatment was cohesive or mixed which indicates a superior adhesion at the interface.

The resistance to peel of the laser treated joints was higher or similar to that of the anodized treated specimen for the adhesive FM73, FM300 2K and FM350NA, respectively.
The highest resistance to peel was achieved for FM73 and its value was ten times higher than that of FM350NA and FM300 2K,probably because FM73 adhesive is more ductile. Failure mode for laser treated adherends after the peel test was cohesive or mixed.

Laser treatment also improved the tensile strengths in comparison to untreated specimen and attained values of 92% , 85% and 89% of the tensile strength of anodized specimens (for FM73 and FM3002K and FM350NA, respectively).

Durability of the laser treated joints was studied by three methods: wedge conventional tests, humidity/heat resistance and resistance to extreme temperatures.

- The durability of the laser treated specimen was better than the untreated joints which totally opened and close to that of the chromic acid anodized adherends joints.
The joints bonded with the adhesive FM73 showed best durability .
- The shear strength of laser treated adherends and of anodized specimen did not deteriorate after 10 days in humidity chamber (95%RH,60°C) compared to the untreated adherends joint which degraded by 27% in strength.

- Testing at extreme temperatures showed a significant advantage of the laser treated joints compared to non treated or anodized ones.

Chemical changes on the Al surface due to laser treatment at different conditions were observed. The results indicate different processes occurring at various laser parameters (energies and times of irradiation).
- FTIR and Auger spectroscopy indicated the formation of various oxide on the surface and a cleaning process of the surface from contaminants and natural oxides.
- Contact angle (with water) on Al decreased as a result of laser treatment,including better wetting .
- At low laser energy $0.18 J/p*cm^2$ ablation of organic contamination and oxidation of Al and Mg occurred without morphological changes due to mostly photochemical ablation and photo-oxidation reactions.
- At energy density below $1 J/p*cm^2$, and above $0.5 J/p*cm^2$ an oxide layer was formed on the surface. At $1 J/p*cm^2$ the laser energy density was high enough to produce surface smoothening. Higher laser energy ($2.7 J/p*cm^2$) resulted in massive plasma formation, an increased surface roughning and nitridation lowering adhesion strength.

It can be concluded that the ArF excimer laser is an effective surface preadhesion treatment for Al adherends with various adhesives as was evaluated earlier for thermoplastic adherends (polyetherimide,polycarbonate and composite PEEK) (9,10).
Furthermore surface treatment for bonding Al adherends with structural adhesives involve the use of harsh chemicals such as acids bases and organic solvents.Laser surface irradiation can therefore be used as an alternative, ecologically favorable treatment.

5. CONTINUATION OF THE PROJECT: January 1st, 1995 -December 31st, 1995

In the proposed investigation prebond surface treatment of copper with excimer laser will be tested and evaluated.

Laser prebond treatment of Al alloys at controlled atmosphere will be conducted and the affect on Al surface and shear strength with structural adhesive will be investigated.
In order to investigate the effect of the environment on laser treatment a vacuum system was designed and ordered.

The following goals will be carried out:

1. <u>Surface treatment of copper at various laser parameters (Jan. 95 -28.2.95)</u>

   Surface treatment of copper with laser at various parameters: correlation between laser parameters with adhedive shear strength in order to achieve maximum shear strength with two adhesives (epoxy filled and modified epoxy formulation).

2. <u>Investigation of the effect of laser treatment on copper surface morphology and chemistry. (1.3.95 -30.4.95)</u>

   Investigation of the effect of laser treatment of copper by SEM, FTIR, Auger and contact angle.

3. <u>Application of water based primers, following laser treatment (1.5.95 -30.6.95)</u>

   Several water based primers: various silane primers would be applied after laser treatment of Al and their effect on the shear strength will be investigated.

4. Investigation of the effect of various atmosphere during laser prebond treatment of Al (1.7.95 -30.10.95)

Experiments in controlled environment on prebond treatment by excimer laser irradiation of Al. Correlation between laser i irradiation parameters and adhesive shear strength (SLS) with the adhesive FM73 or modified epoxy adhesive.

4a. In inert gases:Ar, N^2.

4b. In oxidizing atmosphere: O^2.

4c. In chemical active gases: NH_3, H_2O.

5. Investigation of the effect of various atmosphere on Al surface (1.11.95 - 30.12.95)

Surface chemistry and morphology after laser treatment in controlled environment will be studied by SEM, FTIR, AUGER (ESCA) and contact angle.

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APPENDIX A

Table 3.1(stage 2): Adhesive shear strength for three structural adhesives - primer BR127.Laser energy 180mj/p*cm^2

SAMPLE	PULSE NO.	ADHESIVE	S.L.S Kg/cm^2	FAILURE MODE
UNTREATED		FM300K	39.5±3	a
ANODIZED			305.6±25	m
LASER TREATED	600		88.0±8	a
	1000		86.8±20	a
	2000		101.3±15	a
UNTREATED		FM73	127.7±19.4	c
ANODIZED			428.6±5.7	c
LASER TREATED	600		286.8±16.4	m
	1000		280.5±15.5	m
	2000		286.9±4.6	c
UNTREATED		FM350NA	55.2±5.3	a
ANODIZED			264.1±15.3	c
LASER TREATED	600		92±8.7	a
	1000		86.1±12.5	a
	2000		77.5±5.5	a

c - cohesive failure

a - adhesive failure

m - mixed failure

.../.

Table 3.2 (stage 2): Adhesive bonding shear strength - adhesive FM73, primer A187- with and without oxygen during laser irradiation. Laser energy 180mj/p*cm^2.

SAMPLE	PULSE NO.	ADHESIVE	S.L.S Kg/cm^2	FAILURE MODE	
UNTREATED		FM73	303.4±6.4	c	
ANODIZED			393.9±18	c	
LASER TREATED	100		301.4±1.7	c	WITHOUT OXYGEN
	600		316±15.8	c	
	1000		334±10.7	c	
	2000		319±9.6	c	
LASER TREATED	100		310.7	c	WITH OXYGEN
	600		298.4±2.2	c	
	2000		298±7.6	c	

c - cohesive failure
a - adhesive failure
m - mixed failure

.../.

Table 3.3 (stage 2): Adhesive bonding shear strength -adhesive FM73, primer fresh BR127.

SAMPLE	PULSE NO.	ADHESIVE	S.L.S Kg/cm^2	FAILURE MODE
UNTREATED		FM73	127.7±9.4	c
ANODIZED			428.6±1.7	c
LASER TREATED	1000 $180mj/p*cm^2$		329.6±12	c
	100 $1J/p*cm^2$		312±29	

c - cohesive failure
a - adhesive failure
m - mixed failure

Table 3.4 (stage 2): Adhesive bonding shear strength -adhesive FM73, without primer.Laser energy $180mj/p*cm^2$.

SAMPLE	PULSE NO.	ADHESIVE	S.L.S Kg/cm^2	FAILURE MODE
ANODIZED	--	FM73	370±7.7	c
LASER TREATED	600	FM73	302±15	c
	1000		302±14	c
	2000		321±4.5	c

c - cohesive failure

.../.

Table 3.5 (stage 2): Adhesive bonding shear strength for three structural adhesives primer A187. Laser energy $180 mj/p*cm^2$

ADHESIVE	FM73	FM3002K	FM350NA
SAMPLE	S.L.S Kg/cm^2	S.L.S Kg/cm^2	S.L.S Kg/cm^2
UNTREATED	303.4±6.4(C)		103±3(A)
ANODIZED	393.9±18(C)		249±17(A)
LASER TREATED			
1000 PULSES	325.7±28(C)	294.5±7(C)	217±29(A)
2000 PULSES	344.3±12.8(C)	207±30(C)	190±5(A)
5000 PULSES	330.5±13(C)	289±32(C)	182±28(A)

c - cohesive failure

a - adhesive failure

m - mixed failure

Table 3.6(stage 2) : Effect of Interval Period between Irradiation and Adhesive Bonding. (Adhesive FM73,laser energy $180mj/p*cm^2$,2000pulses.)

SAMPLE OPEN TIME days	PRIMER A187 SLS Kg/cm^2	WITHOUT PRIMER SLS Kg/cm2
1	328±13 (c)	275±12 (70%c)
3	344±13 (c)	321±5 (70%c)
4	322±4 (c)	300±9 (70%c)
10	303±3 (c)	302±17 (70%c)
15	321±12 (c)	296±3 (80%c)
20	306±6 (80%c)	266±14 (60%c)

Table 3.9 (stage 4): Shear strengths of Al joints (adhesive FM350NA, primer BR154).

Surface Treatment	Laser energy at 30Hz $mj/p*cm^2$	Scann. velocity mm/min	No. of Pulses	Shear Strength kg/cm^2	Failure Mode
Untreated				124+20	a(in primer)
anodized				231+37	a(in primer)
Laser treated	180	54	100	133±12	"
	"	10.8	500	149 ±8	"
		8.9	600	153±4	"
	"	5.4	1000	141±9	"
	"	2.7	2000	126±24	"

c - cohesive failure a - adhesive failure m - mixed failure

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